

# Determination of Henry's Law Constants using Internal Standards with Benchmark Values

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## **Abstract**

It is shown that Henry's law constants can be experimentally determined by comparing headspace content of compounds with known constants to interpolate the constants of other compounds. Studies were conducted over a range of water temperatures to identify temperature dependence. The Henry's law constants for a suite of mostly labeled compounds intended for use as internal standards were determined and these internal standards were then used to determine the constants for 90 compounds. This approach was found to correlate well with average of published values for the compounds in the study (0.99) and a very good correlation (>.99999) when compounds had measurements from more than two sources.

Key words: Henry's law constant, temperature dependence, headspace, volatile organic compounds (VOC)

## **Introduction**

The Henry's law constant (HLC) is an important parameter used to describe the potential of a chemical for atmospheric transport. A compound dissolved in water at infinite dilution will partition between the air and water as described by its HLC. The HLC (solubility form) for a compound can be expressed as its concentration in the liquid phase ( $c_l$ ) divided by its partial pressure ( $p$ ) in the vapor phase or

$$HLC = \frac{c_l}{p} \quad (1)$$

The HLC can be determined by independently measuring a compound's vapor pressure and water solubility, measuring its concentrations in water and gas phase at equilibrium, or measuring its concentration in one phase during an equilibrium process<sup>1</sup>. Some of the experimental approaches to determine HLC include batch stripping<sup>2</sup> and static headspace<sup>3,4</sup>. There is generally good agreement among the literature values for HLC; however, there are instances where the data are inconsistent or unreliable<sup>5,6</sup>.

It was noted in a review of HLC in the literature that values would vary 20-30% and that estimating temperature dependence was quite unreliable<sup>5</sup>. It was further recommended that the temperature dependence of HLC should be experimentally determined rather than estimated. Therefore, it is an important undertaking to have an experiment that can easily determine a multitude of compounds at various temperatures. In this work, an approach is undertaken that can determine the HLC for a multitude of compounds simultaneously by using compounds with established HLC values as benchmarks. Comparing amounts in the liquid and vapor phase is simpler using the dimensionless form of Henry's law constant ( $H'$ ) as follows

$$H' = \frac{c_g}{c_l} \quad (2)$$

Where the concentration of compound in the aqueous phase is  $c_l$  and the concentration in the gas phase is  $c_g$ . In a closed system, the mass of compound present in the vapor phase (headspace) is directly related to  $H'$  as

$$H' = \frac{X_0}{M_0 - X_0} \cdot \frac{V_l}{V_g} \quad (3)$$

Where  $M_0$  is the total mass of compound in the system,  $X_0$  is the mass in the vapor phase at equilibrium and  $V_l$  is the volume of the liquid phase and  $V_g$  is the volume of the gas phase. If a fraction of the headspace is removed, then only a fraction of the mass in the headspace is taken as well and it can be expressed as

$$\frac{\Delta V}{V_g} \cdot x_0 = F_0 X_0 \quad (4)$$

Where  $F_0$  is the fraction of headspace ( $V_g$ ) that is sampled. In this work, the headspace is sampled by evacuation and trapping of vapor followed by GC/MS analysis. Because the headspace is not a fixed volume (e.g., syringe volume), the amount of headspace removed for analysis is expressed as  $\Delta V$ .

The mass of a compound taken in the headspace aliquot can be expressed as recovery using either mass or response. Should the recovery be determined by mass, recovery is simply the mass of the compound in the headspace aliquot compared to the total mass in the system. Using responses the recovery would be the instrument response for the aliquot taken compared to the response for the total amount of compound or the sum of responses if a series of headspace samples are taken until no more compound is detected. That is

$$Recovery = \frac{mass_1}{M_0} = \frac{response_1}{\sum_{i=1}^n response_i} \quad (5)$$

where  $mass_1$  is the amount of compound in the headspace aliquot and the responses are as produced by analysis (in this case a mass spectrometer) are linear to mass.  $F_0$  can be solved in terms of recovery and  $H'$  resulting in

$$F_0 = Recovery \frac{H' + \frac{V_l}{V_g}}{H'} \quad (6)$$

The  $H'$  of an internal standard can be used to determine  $F_0$  using eq 6. Once  $F_0$  is established eq 6 can translate recovery into  $H'$  as shown by eq 7.

$$H' = \frac{Recovery}{F_0 - Recovery} \cdot \frac{V_l}{V_g} \quad (7)$$

The use of internal standards to determine  $H'$  has been demonstrated over a narrow range of  $H'$  (7). In this work, a suite of internal standards are used to represent an expanded range of values. One facet of this study is to test the use of internal standards to determine  $F_0$  with the potential to use  $F_0$  to determine  $H'$  for other compounds. Another approach is to use the suite of internal standards to define a function of recovery to  $H'$  and then use the function to determine  $H'$  other compounds.

One hundred twenty three compounds were used in this study. Sixty seven of these compounds had reported HLC values (mole/kg\*bar with dependency) with temperature dependencies in the literature and compiled by Sander<sup>8</sup>. Of these compounds only 26 had more than two sources for HLC values and a deviation of the results no more than 15% (25 °C). These values were not well distributed about the

range of HLC that were of interest so that one phase of work was to identify and determine the HLC for a representative group of compounds. These internal standards were chosen as having representative HLC values from hydrophobic to water miscible and the compounds (mostly labeled) would not be expected to be present in matrices that might be investigated in future studies.

Throughout this study the experimental results for Henry's law constants are expressed as HLC (mole/kg\*bar) to match the Sander database dimensions. The set of experimental HLC (at 298K) are correlated to the set of their database values (averaged) as a measure of how reliable the internal standard approach performed.

## Experimental

**Vacuum Distiller:** A Cincinnati Analytical Instruments Model VDC1012 vacuum distiller (Indianapolis, IN) performed the evacuations in the study and simultaneously concentrate the compounds removed from the 100-mL round bottom vessels. 5 or 50-mL water samples containing the analytes were evacuated with the condenser at 125 °C and the cryotrap at -150 °C. The evacuation time was limited to prevent excessive water from being transferred with the compounds; therefore, only 0.01 and 0.05 min evacuation of the sample chamber was performed. Evacuation continued for 3 min after the sample chamber was closed to complete the transfer of compounds to the cryotrap. The condensate was heated to 110 °C during a 2.5 min transfer to the GC/MS through the transfer line held at 200 °C. The multiport valve was heated to 200 °C and all internal transfer lines heated to 125 °C.

**GC/MS:** The vacuum distiller was interfaced to a GC/MS so that the vacuum distillate is transferred directly to the GC/MS. In this study, the GC/MS was a Thermo DSQ mass spectrometer and Trace GC (ThermoElectron Corp., Austin TX). The GC capillary column was a 30 m x 0.25 mm i.d., 1.5 µm film VOCOL (Supelco, Bellefonte, PA). The GC operating conditions were 2.5 min at -35 °C, 40 °C/min ramp to 60 °C, 5 °C/min ramp to 120 °C and held at 120 °C for 1 min, 20 °C/min ramp to 220 °C and held for 12 min resulting in a GC run time of 34 min. The injection was split 40:1 with a constant flow rate of 1.4 ml/min. The mass spectrometer scanned between 35 and 300 amu at 1 scan/sec.

**Samples:** The sample vessel containing 5 mL water with the compounds being studied was immersed in a water bath. The temperature of the water during equilibration was varied between 0 and 60 °C ( $\pm 0.5$  °C) to determine temperature dependence. The sample vessel contained most of the headspace (~100 of 127.8 mL) with the exception of the o-ring joint and heated sample port. Both water bath and water sample were continuously stirred during the process. Prior to each evacuation, the solution and headspace above the sample are equilibrated for more than two hours. The headspace is evacuated and condensed in the distiller cryotrap and analyzed. The equilibration/evacuation is repeated for a total of eight evacuations (system pressure dropping with each aliquot). Two blanks were analyzed before the first evacuation and between each evacuation. This was done to monitor background and to allow for the system to re-equilibrate (~ 130 min). A set in this work relates to the series of evacuations of a sample that is used to determine the recoveries of compounds in the first evacuation as described by eq 5.

## Results and Discussion

One of the initial problems encountered was how to best determine the total response necessary to determine recovery as identified in eq 5. For compounds that were depleted from the water after 8 evacuations, the total response was simply the sum of responses for the 8 evacuations. In a few instances, the compound could be extrapolated to depletion within 11 evacuations and so the total response incorporated extrapolated responses to depletion. Compounds that were very water soluble required numerous evacuations and for these compounds recovery was determined as the response of the compound compared to its total response when evacuated without water present (1/20 of spike amount). This approach was not ideal as the standard response for these miscible compounds were found to have a deviation  $> 10\%$  which would increase uncertainty in the calculated recovery which would, in turn, impact the interpolated  $H'$ .

By using *select* Sander database compounds (those having three or more results with less than 15% standard deviation) and their experimental recovery,  $F_0$  is determined by eq 6. However, the determination of  $F_0$  was not constant across the range of  $H'$  and somewhat more erratic at the very low recovery range (Fig 1) demonstrating a single value of  $F_0$  to determine  $H'$  would not be reliable. It was therefore more desirable to view the relationship of  $\ln(H')$  or  $\ln(\text{HLC})$  to recovery for each set; therefore, graphing the recoveries vs HLC was used to interpolate HLC. Fig 2 shows the natural logarithm of the average HLC *select* compounds from the Sander database compared to their recoveries. Therefore with the recovery of a compound determined its HLC can be interpolated from a line representing the data.

To assist in the interpolation the equation fitting program (TableCurve 2D® 5.01.01, Systat Software Inc., San Jose, CA) was used to generate the results in this study.

The results for each set were generated in 4 ways. The first and second approaches of plotting  $\ln(\text{HLC})$  to recovery used the same set of data. The first approach was to graph natural logarithm of HLC to total recovery. The second was similar to the first but without the most volatile compounds. Using these two approaches made fitting the data less difficult. When results from the second approach overlap results from the first, an average value was taken. The third approach was only used when compounds had a lower affinity for partitioning into the headspace than the internal standards and therefore necessitated extrapolation. In these instances the internal standards, acetone- $\text{C}^{13}$ , 1,4-dioxane- $d_8$ , and 2-chloroethanol- $d_4$  were used to describe the  $\ln(\text{HLC})$  to recovery relationship. This approach was only viable when the compound recoveries were well behaved and a line could describe with a better than 95% correlation. The fourth approach was simply to base the recovery upon only the 8 evacuations even if this sum was far less than the total should be based on the response of the standard. Generally, the fourth approach for relating  $\ln(\text{HLC})$  to recovery was used for compounds that could not be determined by the first two approaches. It is important to note that there were few instances (3%) where the response generated by analyzing a standard (without water) was used in the calculation of HLC.

The calculated results from these different approaches did vary with experimental conditions. For instance, the hot water samples ( $>40\text{ }^\circ\text{C}$ ) volatilized most compounds so effectively that almost all compounds were eliminated from the vessel with 8 evacuations while the near freezing water ( $1\text{ }^\circ\text{C}$ ) held most compounds so strongly that 8 evacuations would completely remove only a few of the compounds. With warmer water temperatures the impact of  $\ln(\text{HLC})$  on recovery was not easily distinguished as most compounds (wide range of HLC values) were essentially completely in the headspace. Therefore, to reduce the fraction of volatile compounds in the headspace, a larger water size (50 mL) was used to determine their HLC.

The criteria for selection of internal standards to be used in determining HLC values were their not being commonly found in the environment and that they represented a wide range of values. 40 compounds were evaluated as potential internal standards (Table 1). The deuterated compounds required the

determination of HLC as deuterium would be expected to influence volatility and solubility differently than hydrogen atoms; even the deuterated analogs (e.g., benzene- $d_6$ ) of well established compounds like benzene required determination<sup>9</sup>. Once the HLC for each internal standard was established, these values would be used to determine the HLC for the study compounds.

The HLC for the internal standards were determined graphically using compounds in the Sander database that met the criteria for which there were at least three temperature dependent results and the standard deviation for the values was less than 15%. 26 compounds meet these conditions at 23 °C while only 14 compounds meet the criteria at 47°C. These compounds were not well distributed over the range of values for the internal standards and therefore, 4 additional compounds (1,4-dioxane, bromoform, 1,1,2,2-tetrachloroethane, and 1,2,3-trichloropropane) were included. Figure 2 shows recoveries of the compounds with their recoveries for the first series run (23 °C). The four compounds used as reference values that did not pass the criteria are identified as the square data points on the graph.

Eight sets (8 evacuations each set) were used in the calculation of HLC for the internal standards. The temperatures for the evacuations were 1, 21.5(2), 23, 37, 40, 47, 53, 58, and 60 °C. There was difficulty in making a distinct recovery to HLC relationship at the higher temperatures (due to most compounds having equivalent high recoveries) so additional sets were added. Two sets at 38 and 52 °C were performed using only 0.01 min evacuations. There were no advantages observed for the 0.01 min evacuations and the smaller evacuation volume taken diminished the response of compounds. Next, two sets of 0.01 min evacuations were performed using 50 mL water with temperatures 40 and 53 °C and these clarified the  $\ln(\text{HLC})$  to recovery relationship for the more volatile compounds.

The HLC results for the internal standards are presented in Table 1. Comparing the HLC by temperature yielded an average correlation of 0.98 for a temperature range 1 to 58 °C. Two compounds were not as reliable due to their having cross contamination in blanks greater than 1% of their response in headspace (1-methylnaphthalene- $d_{10}$  and pyridine- $d_5$ ).

All of the compounds being investigated as internal standards were ultimately not used as internal standards and those not used might be useful to monitor determinations. Surrogates are identified in Table 1 compounds that can be used to for verify HLC determinations using the internal standards. Their elimination as internal standards was due to their redundancy within the range of values

represented by the chosen internal standards and a potential for problems due to their elevated boiling points (>206 °C).

After the HLC for the internal standards were determined, their recovery versus  $\ln(\text{HLC})$  were graphed as shown in Fig 3. The internal standards recovery to  $\ln(\text{HLC})$  graphs were used to interpolate HLC values for the compounds in the study as listed in Table 2. Using the same sets of evacuations used to generate HLC for the internal standards, the averaged results are listed in Table 2. Acetone and 2-butanone could not be determined due to elevated background levels.

The experimental HLC compare well to the Sander data base HLC values. There is a correlation of .99 for all data where there is at least a single measurement reported in the database. Comparing the experimental HLC to those compounds in the database averages when there are 3 or more sources HLC yields a .99999 correlation.

After the concept of using internal standards was demonstrated additional sets of evacuations were performed using the internal standards and another suite of compounds (identified in Table 2). These additional compounds (isopropyl alcohol, 2-methyl-2-propanol, propargyl alcohol, 2-methoxy ethanol, 2-butoxyethanol and 2-ethyl-1-hexanol) are used as surfactants and dispersants that might migrate to the environment. Glutaraldehyde had been included with the additional compounds but it was found to be too reactive in water to be determined. The HLC values were determined using water temperatures of 0.1, 25, 38, and 59 °C. Their results are included in table 2.

The HLC of both internal standard and surrogate compounds were also determined using the same criteria as for the other compounds. The internal standard experimental HLC values should fall within 10% of the values listed in Table 1. When these limits were exceeded, the experimental results became less reliable as noted for the more volatile compounds in sets where 5 mL of water was heated. The experimental values of the surrogates *o,o*-dichloro-*o*-xylene, pyridine-*d*<sub>5</sub>, 3,5-di-*tert*-butyltoluene, and decafluorobiphenyl were erratic and did not always compare well with the values in Table 1. The remaining surrogate values were more consistent and their experimental results generally fell within 20% of the values contained in Table 1.

The total response from analyzing a standard in an empty vessel was primarily used to show the trends in Figs 1-3 where the recoveries were less than 10%. Because the empty vessel response of a standard was rarely used to determine HLC, it is shown that it is now possible to determine HLC for a compound without actually knowing the amount of the compound in solution. This allows using lesser grade reagents or even a sample containing an unidentified compound to determine HLC.

Generally the interpolation of internal standard HCL values yielded values with confidence intervals between 10-15% exceeding the standard deviation for most of the Sander database HLCs. The uncertainty for the internal standard HLC was equated to the standard error of the line relating HLC to temperature.

The curves generated from the internal standard HLCs had standard errors very similar to those used for calculating the HLC for the internal standard. Combining the interpolated data to describe the temperature vs. HLC line yielded standard errors typically greater than the standard errors (and confidence intervals) of each data point.

Generally the larger relative errors are associated with the most hydrophobic compounds, most hydrophilic compounds and those with the higher boiling points. The more hydrophobic compounds were mostly in the vapor phase and recoveries were always very high and determination of HLC was sometimes influenced by very small changes in recovery. The more hydrophilic compounds had low recoveries, the confidence intervals of their interpolated data points had greater confidence intervals, and their chromatographic resolution the lowest for the compounds in the study. The highest boiling compounds had an elevated memory in the system and transfer from sample headspace to GC/MS would be more prone to losses.

## **Notice**

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**Table 1 Average Henry's Law Constants Determined for Internal Standards and Surrogates**

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	HLC <sup>a</sup>	
Amount <sup>c</sup>	HLC @298 K	Temperature

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Compound	Use <sup>b</sup>	(ng)	(mol/kg·bar)	U <sup>d</sup>	Constant
diethyl ether- <i>d</i> <sub>10</sub>	i	1250	1.314	0.342	6535
acetone- <sup>13</sup> C	i	15500	31.10	2.19	5278
methylene chloride- <i>d</i> <sub>2</sub>	i	1250	0.379	0.054	4564
nitromethane- <sup>13</sup> C	i	3250	48.52	14.38	5029
hexafluorobenzene	i	1250	0.055	0.004	5204
tetrahydrofuran- <i>d</i> <sub>8</sub>	i	1250	23.49	8.20	8036
ethylacetate- <sup>13</sup> C	i	12500	7.165	1.538	6534
pentafluorobenzene	i	1250	0.075	0.005	4762
benzene- <i>d</i> <sub>6</sub>	i	1250	0.181	0.022	3979
1,2-dichloroethane- <i>d</i> <sub>4</sub>	i	1250	0.870	0.071	4299
fluorobenzene	i	1250	0.162	0.017	3882
1,4-difluorobenzene	i	1250	0.163	0.017	3862
1,2-dichloropropane- <i>d</i> <sub>6</sub>	i	1000	0.358	0.042	4584
1,4-dioxane- <i>d</i> <sub>8</sub>	i	12000	278.0	84.4	6832
toluene- <i>d</i> <sub>8</sub>	i	1250	0.197	0.026	4276
pyridine- <i>d</i> <sub>5</sub>	none	62500	417.2	197.2	10204
1,1,2-trichloroethane- <i>d</i> <sub>3</sub>	i	1000	1.304	0.231	5073
1,2-dibromoethane- <i>d</i> <sub>4</sub>	i	1250	1.589	0.332	4848
chlorobenzene- <i>d</i> <sub>5</sub>	i	1250	0.360	0.060	4472
<i>o</i> -xylene- <i>d</i> <sub>10</sub>	i	1250	0.304	0.059	4708
4-bromofluorobenzene	i	1250	0.533	0.123	4437
bromobenzene- <i>d</i> <sub>5</sub>	i	1250	0.651	0.108	4157
1,2-dichlorobenzene- <i>d</i> <sub>4</sub>	i	1250	0.819	0.175	4201
decafluorobiphenyl	none	1250	0.674	0.403	3560
nitrobenzene- <i>d</i> <sub>5</sub>	s	1250	84.93	43.51	7479
acetophenone- <i>d</i> <sub>5</sub>	s	5210	233.2	144.0	10278
1,2,4-trichlorobenzene- <i>d</i> <sub>3</sub>	s	1250	0.979	0.359	4628
naphthalene- <i>d</i> <sub>8</sub>	s	2500	3.484	1.224	5331
1-methylnaphthalene- <i>d</i> <sub>10</sub>	s	5250	4.652	1.765	5397
methylcyclohexane- <i>d</i> <sub>14</sub>	i	1250	0.031	0.006	5637
2-chloroethanol- <i>d</i> <sub>4</sub>	s	600000	498.3	238.4	8738
ethylbenzene- <i>d</i> <sub>10</sub>	i	1250	0.202	0.038	4236
1,2,3-trichlorobenzene- <i>d</i> <sub>3</sub>	s	2500	1.465	0.488	4587
3,5-di-tert-butyltoluene	none	5000	0.373	0.120	9122
3,5-dibromotoluene	s	11000	1.741	0.724	4826
azulene	s	12500	14.88	4.35	7764
<i>a,a</i> -dichloro- <i>o</i> -xylene	none	48750	10.41	4.215	11086
vinylchloride- <i>d</i> <sub>3</sub>	i	1250	0.038	0.006	3087
2-butanone- <i>d</i> <sub>5</sub>	i	2500	37.14	9.56	8164
2-hexanone- <i>d</i> <sub>5</sub>	i	2500	16.77	6.28	9044

<sup>a</sup> Henry's law constant with the temperature dependence constant. The HLC for a given temperature T (in K) is equal to (HLC at 298 K) × exp (temperature dependence constant × (1/T-1/298.15 K)).

<sup>b</sup> Use of the compound. Compounds that were used as internal standards are identified with *i* and compounds with potential as surrogates with *s*. If compound was found not viable as a surrogate or internal standard it is designated with *none*.

<sup>c</sup> Amount of compound added to 5 and 50 mL water. The compounds were purchased in mixtures with stated purity of starting materials generally >99%. For purities <98% the amounts reflect corrections for purity.

<sup>d</sup> Uncertainty estimated using Upper error limit converted from the  $\ln(\text{HLC})$  vs. temperature line standard error.

**Table 2 List of compounds with Henry's law constants in mol/kg·bar**

Compound	amount <sup>a</sup> (ng)	Current Study			Sander	
		@298 K	HLC <sup>b</sup> U <sup>d</sup>	constant	HLC 298 K <sup>c</sup> average	dev
dichlorodifluoromethane	500	0.0126	0.008	5476	0.003	0.001
chloromethane	500	0.0792	0.006	2383	0.108	0.019
vinylchloride	500	0.0393	0.000	3193	0.041	0.004
bromomethane	500	0.1266	0.014	2798	0.088	0.102
chloroethane	500	0.0857	0.001	3181	0.085	0.005
trichlorofluoromethane	500	0.0281	0.001	5077	0.011	0.001
diethyl ether	1000	1.137	0.049	6585	0.787	
1,1,2-trichloro-1,2,2-trifluoroethane	500	0.0205	0.007	5695	0.003	
acetone	1000				30.2	4.257
1,1-dichloroethene	500	0.0408	0.006	4636	0.035	0.005
iodomethane	1000	0.1815	0.026	3245	0.166	0.035
allylchloride	500	0.1309	0.021	4496	0.101	0.013
acetonitrile	2000	60.18	25.48	6261	52.36	2.669
methyl acetate	500	11.84	2.71	7493	7.866	
carbon disulfide	500	0.0573	0.006	3815	0.052	0.007
methylene chloride	500	0.4009	0.043	3909	0.418	0.052
MTBE	500	1.670	0.300	9082	1.621	
acrylonitrile	1000	11.83	2.31	6784	11.05	
<i>trans</i> -1,2-dichloroethene	500	0.1023	0.011	4003	0.104	0.006
1,1-dichloroethane	500	0.1985	0.006	3901	0.185	0.015
2,2-dichloropropane	500	0.0443	0.028	7448		
propionitrile	1000	42.84	12.01	6248	27.00	
2-butanone	2000				15.17	7.001
<i>cis</i> -1,2-dichloroethene	500	0.2692	0.025	3816	0.242	0.022
methacrylonitrile	1000	5.453	0.967	6671		
chloroform	500	0.2764	0.035	4453	0.264	0.023
bromochloromethane	500	0.6649	0.048	4716		
cyclohexane	500	0.0318	0.006	5430	0.006	0.000
1,1,1-trichloroethane	500	0.0689	0.006	4023	0.063	0.007
1,1-dichloropropene	500	0.0615	0.002	4226		
carbon tetrachloride	500	0.0497	0.003	4459	0.036	0.004
1,2-dichloroethane	500	0.8195	0.068	4376	0.889	0.062
benzene	500	0.1831	0.028	3844	0.196	0.027
trichloroethene	500	0.1187	0.019	4695	0.112	0.013
methyl cyclohexane	500	0.0318	0.007	5344	0.010	0.000

1,2-dichloropropane	500	0.4286	0.049	4425	0.359	0.035
methylmethacrylate	1000	4.328	1.192	7685		
dibromomethane	500	1.222	0.053	4988	1.065	0.085
bromodichloromethane	500	0.5175	0.008	4651	0.423	0.082
1,4-dioxane	5000	232.1	45.7	6620	202.0	
4-methyl-2-pentanone	2000	9.994	1.758	8696	2.201	
<i>trans</i> -1,3-dichloropropene	2500	0.5821	0.018	4781	0.560	
toluene	500	0.2129	0.074	4393	0.173	0.025
<i>cis</i> -1,3-dichloropropene	2500	0.9569	0.041	5455	0.430	
2-hexanone	1002	15.37	2.75	8595		
1,1,2-trichloroethane	500	1.394	0.097	5400	1.184	0.089
1,3-dichloropropane	500	1.296	0.107	5282	1.007	
tetrachloroethene	500	0.0995	0.019	4589	0.060	0.006
dibromochloromethane	500	1.071	0.069	5267	0.860	0.098
1,2-dibromoethane	500	1.732	0.238	5532	1.307	0.287
chlorobenzene	500	0.3688	0.027	4378	0.285	0.029
1,1,1,2-tetrachloroethane	500	0.4780	0.020	4790	0.400	0.056
ethylbenzene	500	0.2033	0.070	4138	0.131	0.016
<i>m,p</i> -xylenes	500	0.2225	0.060	4348	0.188	0.038
<i>o</i> -xylene	500	0.3202	0.073	4472	0.245	0.051
styrene	500	0.4455	0.041	4632	0.338	0.064
isopropylbenzene	500	0.1396	0.019	4865	0.087	
bromoform	500	2.173	0.458	6306	1.916	0.328
<i>cis</i> -1,4-dichloro-2-butene	2000	3.040	1.233	9372		
1,1,2,2-tetrachloroethane	500	3.335	0.919	7160	2.215	0.343
1,2,3-trichloropropane	500	4.233	1.081	7213	3.556	0.815
propylbenzene	500	0.1880	0.070	4533	0.091	
bromobenzene	500	0.5980	0.027	4256	0.540	0.007
<i>trans</i> -1,4-dichloro-2-butene	2000	3.501	1.188	6557		
1,3,5-trimethylbenzene	500	0.2349	0.047	5124	0.141	
2-chlorotoluene	500	0.3182	0.077	4065	1.096	1.151
4-chlorotoluene	500	0.4071	0.113	4213		
<i>tert</i> -butylbenzene	500	0.1578	0.039	4738		
<i>sec</i> -butylbenzene	500	0.1321	0.039	4584		
pentachloroethane	500	0.5908	0.090	5413		
1,2,4-trimethylbenzene	500	0.3209	0.063	5155	0.151	0.000
<i>p</i> -isopropyltoluene	500	0.1808	0.057	4935		
1,3-dichlorobenzene	500	0.5257	0.092	4826	0.346	0.064
1,4-dichlorobenzene	500	0.5816	0.092	4588	0.346	0.064
<i>n</i> -butylbenzene	500	0.1963	0.083	4488		
1,2-dichlorobenzene	500	0.8016	0.048	4231	0.536	0.043
acetophenone	1000	97.41	27.28	6796	111.1	
1,2-dibromo-3-chloropropane	500	9.743	1.785	7076		

nitrobenzene	1000	63.99	18.40	7520	47.36	
1,2,4-trichlorobenzene	500	1.069	0.252	5124	0.583	0.170
hexachlorobutadiene	500	0.2357	0.107	6176	0.988	
naphthalene	500	3.321	0.815	6102	2.106	0.009
1,2,3-trichlorobenzene	500	1.537	0.092	4833	0.800	
2-methylnaphthalene	1000	3.543	1.016	5546	0.005	0.000
1-methylnaphthalene	1000	4.412	1.242	5854	3.900	
isopropyl alcohol <sup>e</sup>	500	108.6	64.0	8359	131.7	
2-methyl-2-propanol <sup>e</sup>	500	143.2	73.4	7876	70.99	
propargyl alcohol <sup>e</sup>	500	378.2	12.7	7386		
2-methoxyethanol <sup>e</sup>	500	437.6	19.4	7479	0.022	
2-butoxy ethanol <sup>e</sup>	500	350.2	39.3	7657		
2-ethyl-1-hexanol <sup>e</sup>	500	68.92	24.39	11227		
benzyl chloride <sup>e</sup>	1000	1.960	0.023	7213	1.600	

<sup>a</sup> Amount of compound added to 5 and 50 mL water. The compounds were purchased in mixtures with stated purity of starting materials generally >99%. For purities <98% the amounts reflect corrections for purity.

<sup>b</sup> Henry's law constant with the temperature dependence constant. The HLC for a given temperature T (in K) is equal to (HLC at 298 K) × exp(temperature dependence constant × (1/T-1/298.15 K)).

<sup>c</sup> Average HLC with 1 standard deviation of values reported in the Sander database (reference 7). Some of these values are measurements at 298 K without temperature dependence.

<sup>d</sup> Uncertainty estimated as the upper standard deviation converted from the ln(HLC) vs. temperature line standard error.

<sup>e</sup> Compounds added after initial investigation.

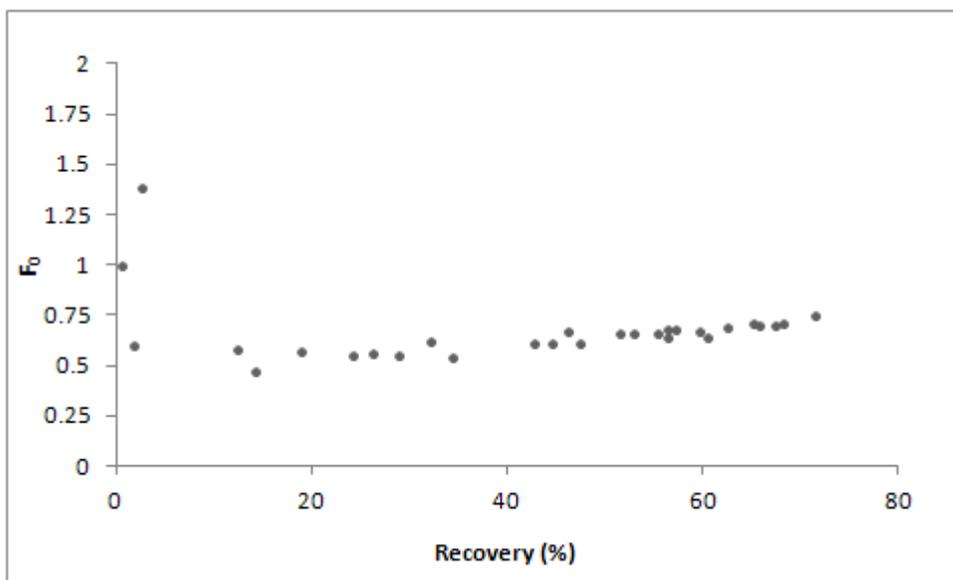


Figure 1 Calculated  $F_0$  for select Sander database compounds at 296 K

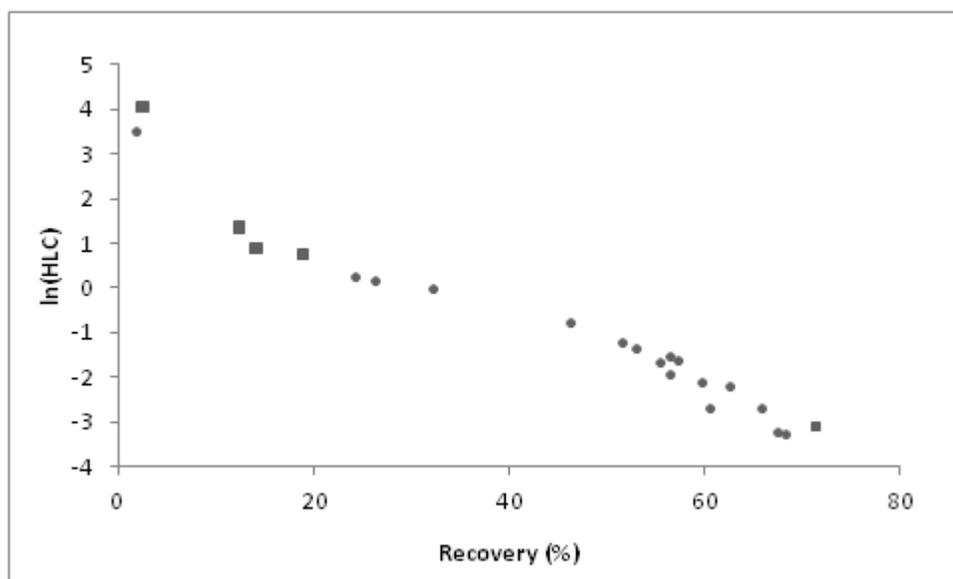


Figure 2 Recovery compared to the  $\ln(\text{HLC})$  for the compounds in Sander database for evacuation at 296 K.

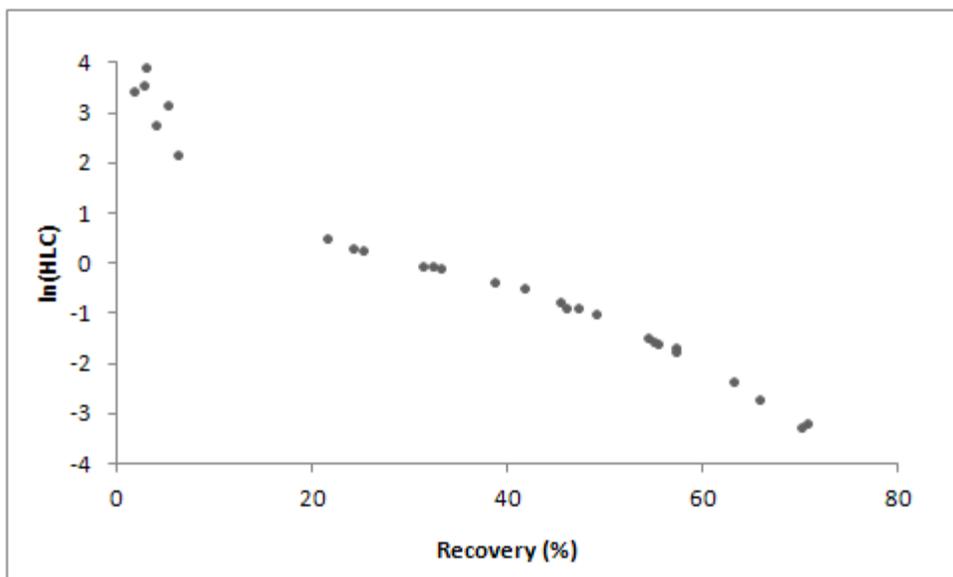


Figure 3 Recovery of internal standards to ln(HLC) used to determine experimental  $H'$  at 296

K.

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