Breath-Alcohol Simulators: Scientific Basis and Actual Performance

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Abstract

Commercial breath-alcohol simulators were studied to determine their suitability as calibrating devices and for providing control specimens in breath-alcohol analysis. The best-fit exponential equation for the air/water partition of ethanol was found to by \( y = 0.0145e^{0.06583x} \), where \( x = \) temperature \(^{o}C\) and \( y = k_{a/w \times 10^3} \). Temperature, volume, pressure, and alcohol depletion of simulators and their effluents were measured. The consequences of temperature fluctuations upon effluent-alcohol concentration were determined, as was the number of times a simulator can be used with various breath-alcohol analyzers before reaching 1% alcohol depletion.

Introduction

The use of controlled-temperature equilibration of alcohol between water and air with breath-alcohol simulators is very widespread in breath-alcohol analysis. As the name implies, simulators were originally developed as training aids to provide surrogate specimens for breath-alcohol analysts. However, they are now widely employed to produce control specimens for checking the proper functioning of quantitative evidential breath-alcohol analyzers and as calibrating devices for such analyzers.

Despite these critical applications of simulators, published information concerning the theoretical basis for their use and actual performance data are scarce. These matters, which are of great significance in laboratory use and field testing of breath-alcohol analyzers and in research on breath-alcohol analysis, were therefore studied in this laboratory.

Theoretical Basis of Ethanol Partition Between Air and Water

The evolution of alcohol vapor from dilute solutions of alcohol under equilibrium conditions is governed by Henry's Law (1), from which it follows that, at definite temperature and independent of pressure,

\[
\frac{\text{Concentration of solute in the liquid phase}}{\text{Concentration of solute in the gaseous phase}} = \text{Constant} \quad (I)
\]

for equilibrium systems of volatile substances in aqueous solution. If a dilute aqueous solution of alcohol is brought to equilibrium with air, the partial pressure of the alcohol in the vapor phase is a function of the alcohol concentration of the liquid phase and of the system temperature. Hence, at constant temperature, the equilibrium alcohol concentration of the vapor phase is controlled by the alcohol concentration of the liquid phase; and at a constant alcohol concentration in the liquid phase, the equilibrium alcohol concentration of the vapor phase is governed by the temperature of the system.

The vapor pressure of a volatile aqueous solute is proportional to the absolute temperature of the system. Thermodynamic consideration for such systems indicate that the logarithms of the air/water Ostwald partition coefficients for alcohol should vary linearly with the reciprocal of the absolute (\(^{o}K\)) temperature. For short temperature ranges of interest for simulators and equilibrators, a direct linear relationship also holds for temperatures expressed in \(^{o}C\).

Experimental air/water partition data for alcohol (or the basis for such data) are contained in seven leading studies published between 1911 and 1974 (2-8). Least-squares, best-fit regression analysis of those data (\( N = 23 \)) yields the following exponential equation governing the equilibrium partition of alcohol between water and air, over the range of temperature interest for equilibrators and simulators:

\[
y = 0.04145e^{0.06583x} \quad \text{(II)}
\]

\[R = 0.999\]

where

\[x = \text{Equilibrium temperature, } ^{o}C\]

\[y = k_{a/w \times 10^3} (= \text{Partition coefficient of alcohol for air/water } x 10^3)\]

\[R = \text{Correlation coefficient}\]

At 34\(^{o}C\), \( k_{a/w \times 10^3} \) = 0.38866. It follows that air equilibrated at 34\(^{o}C\) with an alcohol solution containing 1.226 g alcohol/liter will contain 0.47650 mg alcohol/liter or 100 mg/210 liters. Such an alcohol-in-air specimen should yield a result of “0.100” (i.e., 0.100 g/210 liters) on any breath-alcohol analysis device properly calibrated to reflect an assumed blood-alcohol concentration/breath-alcohol concentration ratio of 2100:1. All seven sets of alcohol partition data for air and water (2-8) are shown in Figure 1 in semilogarithmic presentation, together with the best-fit linear regression line. The linearity of the logarithms of the partition coefficients with temperature and the essentially perfect correlation of the data in the exponential equation II confirm the coincidence of the data with the thermodynamic theory. These data also establish that, at constant temperature and within reasonable limits, the coefficients are independent of the absolute amount of alcohol in the liquid phase of the system, in conformity with Raoult’s law.

Figure 1 and equation II also demonstrate the effect of temperature change on the partition coefficients for this system. Between 33 and 35\(^{o}C\), the coefficients increase by
6.8% per degree. At constant alcohol concentration in the liquid phase, the alcohol content of the vapor phase will, therefore, increase or decrease to the same extent with a rise or fall in system temperature.

**Experimental**

*Breath-Alcohol Analyzers.* Production models of the devices listed in Table I were employed without modification, except for the Model S-11 Breath Tester (Alcohol Countermeasure Systems, Port Huron, MI) which was a prototype unit. All analyzers employed a 2100:1 blood/breath-alcohol calibration factor and were thus calibrated for g/210 liters vapor-alcohol concentrations.

*Breath-Alcohol Simulators.* The following simulators designed for 500-mL alcohol solution volumes and 34°C operating temperatures were employed: Model LS40 Simulator, Luckey Laboratories, Inc., San Bernardino, CA; Model 6000 and Model SK-2 Alcoholic Breath Simulator, Stephenson Co., Red Bank, NJ; and MKII and MKIIA Alcoholic Breath Simulator, Smith & Wesson Electronics Co., Springfield, MA.

*Calcium Sulfate Cartridge Sorption of Alcohol.* Alcohol from vapor-phase specimens collected in the sample chamber of a Model 900 Breathalyzer was sorbed on 0.5 g CaSO₄ cartridges as described by Dubowski (9) and analyzed by automated gas chromatographic headspace analysis.

*Gas Chromatography.* Alcohol was analyzed by automated gas chromatographic headspace analysis with the Multifract F-40 and Model F-45 Vapor Space Chromatograph (Perkin-Elmer Corp., Norwalk, CT) as previously described by Dubowski (10).

**Table I. Typical Simulator Effluent Volumes and Ethanol Depletion/Pass for Various Breath-Alcohol Analyzers**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Model</th>
<th>Mean Effluent Volume, mL</th>
<th>Simulator Outflow Pressure, inches H₂O</th>
<th>Effluent Flow Time, Seconds</th>
<th>Ethanol Depletion¹/ Pass, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol Screening</td>
<td>Device</td>
<td>ASD</td>
<td>1320</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>ALERT</td>
<td>J2A-1000</td>
<td>608</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>ALERT</td>
<td>J3C-R</td>
<td>700</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Breathalyzer</td>
<td>900-A</td>
<td>575</td>
<td>575</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Breathalyzer</td>
<td>1000</td>
<td>510</td>
<td>510</td>
<td>10</td>
<td>10²</td>
</tr>
<tr>
<td>Breath Tester</td>
<td>S-11</td>
<td>1503</td>
<td>1503</td>
<td>25⁴</td>
<td>6</td>
</tr>
<tr>
<td>GC Intoximeter</td>
<td>MK-IV</td>
<td>1121¹</td>
<td>1121¹</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Intoxilizer</td>
<td>4011</td>
<td>4887</td>
<td>4887</td>
<td>7³</td>
<td>38⁶</td>
</tr>
<tr>
<td>Intoxilizer</td>
<td>4011A</td>
<td>4616</td>
<td>4616</td>
<td>8³</td>
<td>31⁶</td>
</tr>
<tr>
<td>Intoxilizer</td>
<td>4011A/</td>
<td>3885</td>
<td>3885</td>
<td>5³</td>
<td>36⁶</td>
</tr>
<tr>
<td></td>
<td>27-10100</td>
<td>1915</td>
<td>1915</td>
<td>5³</td>
<td>19⁶</td>
</tr>
</tbody>
</table>

¹ Calculated for effluent ethanol concentration of 100 mg/210 L yielded by Simulator at 34°C
² Effluent flow maintained for 5 seconds
³ Effluent flow maintained for 10 seconds
⁴ Outflow pressure of 25 inches H₂O was required to achieve sample acceptance
⁵ Effluent delivered into breath inlet tube
⁶ Pressure and flow time internally controlled by instrument in “Calibrator” mode

![Figure 1. In Vitro partition ratio of ethanol for the air/water system as a function of temperature.](image)
EU-200-62 digital electronic thermometer (Heath Co, Benton Harbor, MI) and Model 705 thermoliner probe (Yellow Springs Instrument Co., Yellow Springs, OH). The thermometer and thermistor probe were calibrated against an NBS Standard Reference Material 934 mercury-in-glass thermometer (U.S. Department of Commerce, National Bureau of Standards, Washington, DC). Simulator effluent volumes were measured with a Wright Model MK12 respirometer (British Oxygen Co., Ltd., Pinaccles, Essex, U.K.) and a Dräger Model 2207-10 Volumeter (North American Drager, Telford, PA). Simulators were operated with compressed air, regulated to produce ten inches of H₂O pressure at the simulator outlet, except as noted, with flow rates controlled by the connected breath-alcohol analyzer. Simulator effluent outflow pressures were measured at the simulator outlet with a Model 2050C Magnehelic direct-reading differential pressure gauge (Dwyer Instruments, Inc., Michigan City, IN).

**Simulator Solutions.** Simulators were charged with 0.5 liter of alcohol solutions prepared to yield various target alcohol concentrations of the effluent at 34°C in accordance with equation II, employing \( k_a/w \times 10^3 = 0.38866 \) (e.g., 0.613, 1.226, and 2.452 g alcohol/liter, respectively, to yield effluents containing 50, 100, and 200 mg alcohol/210 liters). The alcohol concentration of all simulator solutions was verified by gas chromatographic analysis before and after use.

**Results**

**Temperature Fluctuation of Simulators**

The results of random and periodic static temperature measurements (i.e., without effluent production) on a series of 34°C simulators are shown in Table I; the simulators remained undisturbed at room temperature (24°C) between measurements. Static temperature measurements on a typical Model 6000 Stephenson Co. 34°C simulator, made consecutively at one-minute intervals for 100 minutes, yielded: Mean = 34.16°C, SD = ±0.095°C, CV = 0.28%, range = 34.01-34.33°C. A histogram of these measurement results with normal curve overlay is given in Figure 2.

| Table II. Temperature Observations on Commercial 34°C Breath-Alcohol Simulators* |
|---------------------------------|-----------------|-----------------|-----------------|
| Simulator | Mfr. & Model | Observed Temperature, °C | Single Random Measurement | Mean of 5 Measurements† |
| 1 | S&W MKIIIA | 34.03 | 34.12 |
| 2 | S&W MKIIIA | 34.02 | 34.06 |
| 3 | S&W MKIIIA | 34.11 | 34.18 |
| 4 | S&W MKIIIA | 34.10 | 34.14 |
| 5 | S&W MKIIIA | 34.04 | 34.16 |
| 6 | S&W MKIIIA | 34.00 | 33.99 |
| 7 | S&W MKIIIA | 34.17 | 34.23 |
| 8 | S&W MKIIIA | 34.14 | 34.19 |
| 9 | S&W MKIIIA | 34.28 | 34.20 |
| 10 | S&W MKIIIA | 34.23 | 34.20 |
| 11 | Stephenson SK-2 | 34.05 | 34.05 |
| 12 | Stephenson 6000 | 33.78 | 33.92 |
| 13 | Stephenson 6000 | 34.19 | 34.08 |
| 14 | Stephenson 6000 | 34.11 | 34.01 |
| 15 | Luckey LS40 | 34.18 | 34.08 |

*Factory specifications = 34 ± 0.2°C
†Temperature measured at 0, 15, 30, 60, 120 minutes

The effect on the theoretical effluent alcohol concentration of the cyclical temperature fluctuations resulting from the normal on-off heating cycle of the simulator is illustrated in Figure 3, in which each of the 101 consecutive static temperature measurements is represented by the corresponding effluent-alcohol concentration for an initial solution alcohol concentration of 1.266 g/liter and assuming no prior depletion of alcohol. Static temperature measurements on the same Model 6000 34°C simulator, made at the beginning of each heating cycle, at every three-minute interval, and at every highest observed value yielded (N = 116): Mean = 34.14°C,
SD = ±0.13°C, CV = 0.38%. The simulator remained undisturbed at room temperature (23.4°C) between measurements.

**Simulator Effluent Volumes and Alcohol Depletion**

Typical simulator effluent volumes for stated simulator outflow pressures are given in Table I for simulators coupled to several quantitative evidential breath-alcohol analyzers and screening test devices. The compressed air flow into the simulator was regulated to achieve ten inches H2O effluent outflow pressure, except when otherwise required by the breath-alcohol analyzer. The corresponding, calculated alcohol quantity lost per test for an initial simulator solution concentration of 1.226 g alcohol/liter and effluent-alcohol concentration of 100 mg/210 liters is also stated in the last column of the table for each single use of the simulator.

The effect of repeated use of a simulator upon depletion of its alcohol content, for various effluent volumes per test, is illustrated in Figure 4. The data for that figure are derived from equation II, and apply to a 34°C simulator. The representation is approximate, since the calculations are based only on the initial alcohol concentration of the simulator solution. Statistical regression analysis of the data yields the following power equation for the depletion phenomenon to the extent of 1% depletion of the alcohol concentration of the simulator solution:

\[
y = 12.87x^{-1}
\]

\[
R = 1.000
\]

where

- \( x \) = Effluent volume/test, liters
- \( y \) = Number of tests yielding 1% depletion from the initial alcohol concentration of the simulator solution
- \( R \) = Correlation coefficient.

The alcohol depletion phenomenon is also illustrated by the data in Table III, which gives experimental results for repeated use of a 34°C simulator with a Model 4011A Intoxilyzer, employing the internal "Calibrator" mode of the instrument which in this instrument produced a 31-second cycle of compressor-produced air flow at a pressure of eight inches H2O measured at the simulator outlet. These data document the progressive decrease in effluent alcohol concentration to a final 92.1% of the initial Intoxilyzer reading, after 25 calibration cycles. For this instrument, from the experimental data in Table I and equation II, the calculated theoretical effect of 25 calibration cycles with the same 34°C simulator would be a reduction in effluent-alcohol concentration to 91.0% its initial value to a final result of 91 mg/210 liters, disregarding the intermediate incremental depletion in the calculation.

**Compensation for Alcohol Depletion in Simulators**

For applications demanding high precision and accuracy, such as calibration of gas chromatographs, substantial improvements in simulator performance can be obtained by using a tandem arrangement of two simulators matched for temperature and charged with the same alcohol solution. Table IV illustrates the effect of tandem-simulator use on improvement of the precision of replicate analyses of alcohol from vapor specimens stored on calcium sulfate cartridges and subsequently analyzed by automated gas chromatographic headspace analysis (10), compared with the capture and analysis of replicate alcohol effluents from a single 34°C simulator. The corresponding mean results, at a 100 mg/210 liters effluent-alcohol target value, were 98.2 and 100 mg/210 liters,
Table IV. Effect of Using Single and Tandem Simulators on the In Vitro Precision of Ethanol Sorption with CaSO₄ Tubes

<table>
<thead>
<tr>
<th>Technique</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single*</td>
<td>SD ±1.35</td>
<td>SD ±2.77</td>
<td>SD ±6.62</td>
</tr>
<tr>
<td></td>
<td>CV 2.7%</td>
<td>CV 2.8%</td>
<td>CV 3.4%</td>
</tr>
<tr>
<td>Tandem†</td>
<td>SD ±0.79</td>
<td>SD ±1.33</td>
<td>SD ±2.13</td>
</tr>
<tr>
<td></td>
<td>CV 1.6%</td>
<td>CV 1.3%</td>
<td>CV 1.07%</td>
</tr>
</tbody>
</table>

*N = 16 replicates
†N = 25 replicates

Discussion

Commonly-encountered directions for use of the 34°C simulator in breath-alcohol analysis, e.g., those in the Breathalyzer Model 900A Instruction Manual (11), call for an alcohol solution concentration of 1.21 mg alcohol/mL (= 1.21 g/liter) to produce an effluent-alcohol concentration of 0.100 g/210 liters which would yield a "0.100" reading on analyzers calibrated in % w/v for a 2100:1 blood/breath alcohol conversion ratio. Instructions for other target effluent-alcohol concentrations use multiples of 1.21 mg/mL. Such directions, which will actually yield an effluent-alcohol concentration of 98.76 mg/210 liters by equilibration with a 1.21 g/liter alcohol solution at 34°C, apparently derive from linear interpolation between 30 and 35°C of the widely distributed data for the air/water partition ratio of alcohol published by Harger, et al. (5). The value for \( k_{aw} \times 10^3 \) at 34°C thus estimated corresponds to a water/air alcohol ratio of 2523:1 compared with a ratio of 2573:1 calculated from equation II, which is based on all data for the air/water partition of alcohol in the seven leading studies (2-8). The latter indicates that a solution-alcohol concentration of 1.226 mg/mL (= 1.226 g/liter) is required to produce an effluent-alcohol of 100 mg/210 liters by equilibration with air at 34°C.

Although the 1.21 mg/mL alcohol concentration differs by only 1.3% from the required 1.226 mg/mL use of the former has a significant, unfortunate effect. Breath-alcohol analyzers are commonly calibrated by designating the effluent obtained from air passage through the 1.21 g/liter alcohol solution at 34°C as nominally containing 0.100 g/210 liters (et cetera for other solution concentrations). The instrument readouts thus over-report the actual vapor and breath-alcohol concentrations and their assumed blood-alcohol equivalents by the same 1.3%. Such overestimation is forensically indefensible, especially at the critical 0.10% w/v breath-alcohol concentration, which is a key decision point in jurisdictions where per se driving-under-the-influence-of-alcohol statutes and in borderline decisions in jurisdictions using the 0.10% w/v BAC presumption for defining the alcohol element of certain traffic offenses.

Equation II and Figure 1 also apply to vapor-alcohol equilibrators at room temperature. Equation II can be used to calculate the actual effluent-alcohol concentration at an observed equilibrator temperature for an equilibrated alcohol solution of known concentration.

The results of the simulator temperature measurements reported here illustrate several problems: Commercial simulators fluctuate significantly in temperature with asymmetrical heating and cooling cycles, their actual operating temperatures occasionally lie outside of the claimed ± 0.2°C limits, and temperature effects alone can cause significant fluctuations in effluent-alcohol concentration. The histogram in Figure 2 shows that static temperatures below the mean in a typical simulator occur more often than temperatures above the mean, because of the rapid, short heating and longer cooling cycles. Table II and Figures 2 and 3 reflect static temperature measurements, i.e., without periodic air flow through the simulator. Air flow induces additional temperature effects, especially if the air temperature is below 34°C. The design of some simulators adds a further adverse temperature-related element—the metal components of the simulator head on standing tend to reach temperatures above that of the solution and heat radiates into the fluid, increasing the headspace vapor alcohol concentration above that for the general liquid-air equilibrium. Preliminary clearing of the headspace vapors before use of the effluent can eliminate difficulty from this source.

The information in Tables I and III and Figure 4 illustrates the possibility of rapid alcohol depletion and the consequent importance of knowing the effluent volume per test required for a given breath-alcohol analyzer. The alcohol depletion per pass for the listed instruments permits an informed decision on how many tests to perform on a single simulator charge of 613 mg alcohol without exceeding a given depletion limit, such as 1% of the original solution alcohol concentration. One percent alcohol depletion appears to be a reasonable limit, especially for calibration, research, and other critical uses. Figure 4, of course, applies only to a 1% alcohol depletion limit, 34°C simulators, and a 500-mL, charge; under those conditions it applies regardless of the concentration of the simulator alcohol solution.

An important factor beyond the scope of this article is the back-pressure of a given combination of simulator and breath-alcohol analyzer. High back-pressures induce artifacts which affect the functional alcohol concentrations of simulator effluents. Use of breath to drive simulators leads to additional variability, and should be discouraged for most purposes. As shown in Table IV, use of identical simulators in series can significantly improve their performance with respect to accuracy and precision of the effluent alcohol content, and is a simple means toward that goal for critical applications.

The foregoing information and considerations lead to certain conclusions and recommendations. Conclusions that can be made include:

- Presently available commercial simulators used singly are not precision calibrating devices and should not be so employed.
- The temperature regulation of some commercial simulators is occasionally and unpredictably inadequate.
- The effect of temperature fluctuations on effluent-alcohol concentration is marked and often unappreciated.
- Use of simulators in tandem offers a simple means of...
improving their performance.

Redesign of simulators for certain applications is indicated, and some commercial simulators require modifications for any use.

The following modifications of existing commercial simulators are suggested:

An enlarged version of the standard commercial simulator (with respect to alcohol solution volume and related features) should be produced for some uses.

A practical means for uniform, complete equilibration of alcohol between air and water, in a single pass, should be installed in simulators (e.g., appropriate glass or ceramic frits).

Control thermometers (distinct from thermoregulators) should be installed in all simulators.

Air inlet and effluent outlet connections should be keyed to prevent inadvertent misconnection.

Simulator heads should be protected from overheating, e.g., by stirrer motors.

All simulators should be provided with an on-off switch and pilot light, separate from that indicating heater function.

More effective means of temperature regulation, such as proportional power application, should be employed.

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References


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