

The Flawed Nature of the Calibration Factor in Breath-Alcohol Analysis

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In recent years, a number of articles have appeared in this *Journal* addressing various aspects of breath-alcohol analysis, including the role of Henry's law in this type of analysis and the variability of the blood-alcohol to breath-alcohol partition ratio (blood:breath ratio, or BBR) central to the conversion of any measured breath-alcohol concentration ($\text{BrAC}_{\text{Meas.}}$) into a corresponding estimated blood-alcohol concentration ($\text{BAC}_{\text{Est.}}$) (1–4). More specifically, within the context of breath-alcohol analysis, Henry's law describes the equilibrium distribution of ethanol vapor between alveolar air and circulating pulmonary blood at 34 °C, the average temperature of such air. When breath analysis is used to determine a subject's $\text{BAC}_{\text{Est.}}$ from his or her $\text{BrAC}_{\text{Meas.}}$, eq 1, derived from Henry's law, is used (2). In this equation, the 2100:1 BBR, reflects the assumption that for all subjects undergoing a breath-alcohol analysis and having an average alveolar air temperature of 34 °C, 2100 mL of this expired air contains the same mass of ethanol as 1 mL of blood.

$$\underbrace{\frac{\text{no. g ethanol}}{100 \text{ mL blood}}}_{\text{BAC}_{\text{Est.}}} = \underbrace{\frac{2100 \text{ mL breath}}{1 \text{ mL blood}}}_{\text{BBR}} \times \underbrace{\frac{\text{no. g ethanol}}{210 \text{ L breath}}}_{\text{BrAC}_{\text{Meas.}}} \quad (1)$$

The Role of Simulator Solutions

A breath-alcohol simulator is an ideal Henry's law system consisting of a dilute solution of ethanol in water maintained at 34 °C. Simulator solutions are intended to simulate human test subjects and are routinely used to check the accuracy of breath-alcohol analyzers that rely on a specific BBR, defined in the United States of America as 2100:1. These analyzers are utilized by law enforcement agencies to determine the alcohol concentrations in samples of alveolar air provided by suspected DWI (driving-while-intoxicated) arrestees. Measured BrACs are reported in concentration units of g ethanol/210 L breath in jurisdictions where legal limits are defined in terms of specific BrACs, for example, 0.08 g ethanol/210 L breath in California. In other jurisdictions, measured BrACs are converted into equivalent estimated BACs via eq 1. So in New York, for example, where the legal limit is 0.10 g ethanol/100 mL blood, or 0.10%, a $\text{BrAC}_{\text{Meas.}}$ of 0.10 g ethanol/210 L breath is equivalent to a $\text{BAC}_{\text{Est.}}$ of 0.10%.

For a simulator solution maintained at 34 °C, the partition ratio corresponding to the BBR would be the water-alcohol to air-alcohol partition ratio ($k_{w/a}$). This ratio has been estimated by Dubowski to be 2573:1, derived from his least-squares, best-fit regression analysis of data documented in a number of relevant studies (5). An equivalent form of the equation stemming from Dubowski's analysis is eq 2, which yields the value of 2573:1 cited above for $k_{w/a}$ when x , the

temperature in °C, is 34 °C.

$$k_{w/a} = \frac{1 \times 10^3}{0.04145 e^{0.06583 x}} \quad (2)$$

Later investigations by Dubowski and Essary (6, 7) and Speck et al. (8) reveal ranges of $k_{w/a}$ whose upper and lower limits do not differ significantly from Dubowski's empirically derived ratio of 2573:1.

Simulator-Based Calibrations

Given that breath-alcohol analyzers rely on a fixed BBR, all test subjects, including simulator solutions, are assumed to be characterized by the same partition ratio. So if a breath-alcohol analysis is conducted on a DWI arrestee in New York, for example, the breath-alcohol analyzer is calibrated with a simulator solution that is expected to generate a result of 0.10% if the analyzer is functioning properly at a fixed partition ratio of 2100:1. This result can be calculated prior to a given calibration using eq 3: R denotes the partition ratio of the test subject, which in the case of a simulator solution is estimated to be 2573:1 at 34 °C; $\text{AC}_{\text{Actual}}$ is the true alcohol concentration of the test subject, which for a simulator solution intended to produce a 0.10% result on a properly functioning breath-alcohol analyzer is 0.1226% (5); and $\text{AC}_{\text{Reported}}$ is the alcohol concentration reported by a breath-alcohol analyzer relying on a 2100:1 partition ratio.¹ Clearly, when 2573 and 0.1226% are substituted, respectively, for R and $\text{AC}_{\text{Actual}}$ in eq 3, the truncated value of $\text{AC}_{\text{Reported}}$ is 0.10%.

$$\text{AC}_{\text{Reported}} = \frac{2100}{R} \times \text{AC}_{\text{Actual}} \quad (3)$$

The NHTSA Conforming Products List

Breath-alcohol analyzers that appear on the *Conforming Products List (CPL) of Evidential Breath Measurement Devices* of the U.S. Department of Transportation's National Highway Traffic Safety Administration (NHTSA) are those devices that have been evaluated for precision and accuracy at certain values of $\text{AC}_{\text{Reported}}$. Specifically, instruments that meet the model specifications established in 1993 (10) and amended in 1994 (11) are those instruments that have been evaluated for precision and accuracy at 0.000 (blank reading), 0.020, 0.040, 0.080, and 0.160% alcohol concentrations, and that generate results within an acceptable systematic error range of $\pm 0.002\%$ ($\pm 2\%$ at a BrAC of 0.10 g/210 L or a BAC of 0.10%). For the blank reading, the regulations require that, "The tester shall use his or her own breath ... and he or she may not consume alcohol for a period of 48 hours prior to this test or smoke for a period of 20 minutes prior to this

test" (11). For the remaining test concentrations, or AC_{Reported} values of 0.020, 0.040, 0.080, and 0.160%, simulator solutions having concentrations corresponding to AC_{Actual} values of 0.0245, 0.0490, 0.0980, and 0.1960%, respectively, would be used. These concentrations can be determined by using eq 3 to solve for AC_{Actual} in each case, in accord with eq 4, with 2573 substituted for R .

$$AC_{\text{Actual}} = \frac{R}{2100} \times AC_{\text{Reported}} \quad (4)$$

The Flawed Nature of the Calibration Factor

The fundamental flaw of simulator-based calibrations is that, while they produce values of AC_{Reported} within an established margin of error when a breath-alcohol analyzer functions properly at 2100:1 (or at another fixed BBR, such as 2000:1 or 2300:1 (12), both of which have been adopted outside the United States), they do not guarantee accurate results when humans undergo breath-alcohol analysis. This flaw occurs because a properly maintained simulator solution is an ideal Henry's law system, as noted above, while a human subject is not. Therefore, calibrations of breath-alcohol analyzers with such solutions deal only with instrument error, one of the three types of systematic error (13). Where human test subjects are concerned, however, those calibrations do not address method error, the second type of systematic error (13), which stems from the nonideal behavior of human subjects and can be significant.² In this regard, Jones (14) reported that 70% of the uncertainty in breath test results is attributable to physiological variables, and Simpson (15) reported that 90% of the uncertainty in breath test results is "ascribable to variables involving the subject." The blanket claim, therefore, that the result of a breath-alcohol analysis reflects the subject's actual BAC within the same narrow margin of error characterizing simulator-based calibrations, is misleading and untenable.

This argument applies as well to calibrations of breath-alcohol analyzers involving dry gas ethanol standards that are also used to simulate breath samples provided by human test subjects. These standards are available as ethanol-in-nitrogen compressed gas mixtures having certified ethanol concentrations that can be expressed in units of g ethanol/210 L gas at 34 °C and 760 torr (16). Dubowski and Essary (16) have confirmed that calibrations derived from such standards generate results consistent with those based on aqueous simulator solutions. The effluent from any of the latter, in contrast to the dry gas standard, is essentially saturated with water vapor and is termed wet gas. Breath-alcohol analyzers capable of utilizing both wet gas and dry gas calibrations are equipped with a barometric sensor to facilitate corrections for barometric pressure variability when the latter type of calibration is used.³

The physiological variables, referred to above, that affect the accuracy of a breath-alcohol analysis involving a human subject are addressed below within the context of breath test results reported in terms of BAC_{Est} . It must be emphasized, however, that these variables apply as well in those cases where breath test results are reported in terms of $BrAC_{\text{Meas}}$. This is a consequence of the fact that direct $BrAC$ statutes in

the United States and elsewhere are based on a 2100:1 BBR (or on the other values of the BBR cited above), a point that Jones has stated explicitly (12) and that Labianca and Simpson (17) have demonstrated unequivocally via a simple mathematical proof.

Variability of the BBR

Extensive data demonstrating BBR variability have been documented in the scientific literature over the years, so only key conclusions stemming from these data and concerning the postabsorptive and absorptive states of alcohol metabolism are emphasized here.

For the postabsorptive state, Dubowski (18) reported normally distributed BBR data characterized by a mean of 2280:1 and a statistical range of 1555:1 to 3005:1 for 99.7% of the drinking population. Based on the standard 2100:1 ratio, it can be shown that Dubowski's data are consistent with a relative error range of -26% to +43%. Moreover, those data reflect a ratio of BAC underestimates to overestimates of 77:23 (15, 19). In contrast, Jones's postabsorptive data (20) indicate a lower, although still significant, ratio of underestimates to overestimates of 69:31 (21).

A noteworthy point in this regard is that the typical wet gas simulator calibration of a breath-alcohol analyzer is an example of an analysis that produces an underestimated result and, furthermore, definitive proof of the inability of such analyzers to adjust for test subjects having partition ratios that deviate from 2100:1. As noted above, a simulator solution whose AC_{Actual} is 0.1226% is expected to generate a truncated AC_{Reported} of 0.10% on a properly functioning breath-alcohol analyzer operating at a BBR of 2100:1. This is obviously a false-low result for the simulator solution in question, but, nevertheless, the anticipated, correct false-low result that would be generated by a breath-alcohol analyzer relying on a partition ratio lower than that of the 2573:1 defining the simulator solution. Moreover, and even more significant because of the adverse societal impact that would ensue, is the hypothetical scenario in which the simulator solution would be a DWI arrestee in a jurisdiction having a legal limit of 0.12%. Although there are no such jurisdictions in the United States, the point is that, such an arrestee, although clearly guilty of DWI, would not be so charged because his or her AC_{Reported} would fall below the legal limit.

For the absorptive state, the effect of BBR variability is substantially more pronounced (22). Mason and Dubowski (23) have emphasized that, "... when blood and breath tests are available to a subject, the breath test can be discriminatory in yielding a higher result than a blood test during absorption." More recently, Dubowski (18) added, "significant variations from [the postabsorptive mean BBR of 2280:1] exist during active alcohol absorption and [as indicated above] in some individuals even in the postabsorptive state." In fact, Labianca and Simpson (24) determined a mean absorptive state BBR of 1836:1, derived from lognormal statistical analysis of the data of Giguere and Simpson (25). The logarithm-transformed data are normally distributed and involve a statistical range of 1128:1 to 2989:1 for 99% of the drinking population in the absorptive state. This reflects a relative error range of -46% to +42% and a ratio of underestimates to overestimates of 24:76. The data of Jones (20) for the absorptive state indicate a less

pronounced, but certainly significant, ratio of underestimates to overestimates of 35:65 (26).

The Effect of Temperature

Consistent with Henry's law is the fact that temperature must be controlled in any given application, and this is certainly the case for simulator solutions maintained at 34 °C, as indicated above. Yet oral temperature measurements of DWI arrestees are not part of the protocol used by law enforcement agencies, despite the fact that such measurements and the use of appropriate corrections where necessary have been endorsed (27–29). In this regard, studies have shown that the BBR changes with temperature by factors ranging from 6.5%/°C (30) to 8.6%/°C (29).

Breathing Pattern

The length of time involved in breath sample delivery is also a critical variable in breath-alcohol analysis. Hlastala (31) has found that errors in $BAC_{Est.}$ of as much as $\pm 50\%$, or more, can occur by altering the breathing pattern. He attributes this variation to changes in alcohol concentration during the breathing process, stemming from cooling and heating of the breath and airways. These dynamics of airway alcohol exchange effect a positively sloped alveolar plateau (32). Thus the longer a test subject exhales into a breath-alcohol analyzer after breathing the cooler air of the surroundings, the greater the positive deviation from the true BAC. Hlastala (31) offers the example of a $BAC_{Est.}$ of 0.14% stemming from a lengthy breath sample delivery that would be consistent with a significantly lower BAC of 0.09%, where the former concentration is nearly 50% more than the latter. Ohlsson et al. (33) also reported an increase of over 50% in the $BrAC_{Meas.}$ of a subject with a large vital capacity (6.3 L) who exhaled into the infrared-based breath-alcohol analyzer used in the analysis well beyond the required minimum breath delivery time of 4 s at a pressure exceeding 11 torr.

The effect of breathing technique on the results of breath-alcohol analyses has also been explored by Jones (30). He found that, with breath-holding for 30 s prior to exhalation, $BrAC_{Meas.}$ and breath temperature increased by as much as 18% and 0.7 °C, respectively. On the other hand, hyperventilation for 20 s prior to exhalation produced decreases in $BrAC_{Meas.}$ and breath temperature of up to 12% and 1.2 °C, respectively.

Other Variables

The health of a subject undergoing breath-alcohol analysis is another important consideration that cannot be ascertained by a breath-alcohol analyzer deemed to be accurate based on a simulator calibration. A specific example in this regard is a case described by Labianca and Simpson (17), which involved a severely asthmatic defendant charged with DWI in California. The charge stemmed from a $BAC_{Est.}$ of 0.09% at a time when the statutory legal limit in California based on breath tests was 0.08% (as indicated above, California currently has a direct breath statute in place that specifies an equivalent legal limit of 0.08 g ethanol/210 L breath). The defendant presented evidence at his trial—derived from controlled experiments conducted after he was charged and involving the analysis of samples of his blood- and breath-alcohol that were taken essentially simultaneously—that

showed a postabsorptive BBR of 1233:1. With 1233 substituted for R, eq 4 revealed that the defendant's AC_{Actual} was 0.05%, and this led to the ultimate dismissal of the DWI charge. The above case is certainly not unique. As emphasized elsewhere (17), Russell and Jones (34), in their study of subjects with chronic obstructive pulmonary disease—which includes conditions such as asthma and emphysema (35)—concluded that, “quantitative measurement [involving breath-alcohol analysis] must be approached with caution” when test subjects lack effective pulmonary function.

Additional variables that contribute to the uncertainty in results obtained from a properly calibrated breath-alcohol analyzer include mouth-alcohol contamination and contamination of breath samples with compounds that can be mistakenly identified as alcohol. In the first instance, studies on an infrared-based breath-alcohol analyzer, which apparently has the capability of identifying mouth-alcohol from sources such as bleeding gums or regurgitation of stomach contents, produced false-high results and demonstrated that the identifying mechanism is not foolproof (36). In the second case, the same type of infrared-based breath-alcohol analyzer⁴ also generated false-high results. This occurred because of the inability of the instrument to distinguish between the methyl group of ethanol and the methyl group(s) of the solvents toluene and the *o*-, *m*-, and *p*-xylenes to which test subjects had been exposed (37).

Conclusion

Obviously, method error in breath-alcohol analysis is a significant issue, and if the impact of a relevant variable cannot be ruled out in a particular DWI case, then that variable must be taken into account. Clearly, the claim by users of breath-alcohol analyzers that such instruments are accurate because they produce accurate results within a specified margin of error when calibrated with simulator solutions (or dry gas standards) is a very limited claim. The only acceptable point of accuracy in this situation is that the breath-alcohol analyzer that functions properly at a fixed BBR is capable of accurately analyzing such a solution (or dry gas standard). However, when the same breath-alcohol analyzer is used to test a human subject, the result cannot automatically be deemed accurate: it must be evaluated within the context of its uncertainty. We teach our students in various chemistry courses to abide by this protocol when evaluating experimental data, and we can certainly expect agencies that rely on wet or dry gas calibrations of breath-alcohol analyzers to abide by it as well.

Moreover, it is important to place the message of this article into a broader, general context. That is, a calibration standard should, ideally, mimic the composition of the sample to be analyzed (38). Thus, for example, if a particular sample is to be analyzed for a metal ion via absorption analysis of a colored complex ion derived from the metal ion, the presence of sulfate and phosphate ions in the sample matrix can interfere with the analysis. Sulfate and phosphate ions have a tendency to form colorless complexes with metal ions; as a consequence a significant reduction in the concentration of the desired colored complex ion and its associated absorbance can occur for the sample in question. To offset this type of matrix effect, calibration standards can be used that contain

sulfate and phosphate ions in amounts similar to those characterizing the sample matrix (38).

Skoog et al. (39) offer other examples consistent with the above argument concerning calibration standards and their utility in the analyses of unknown samples. For breath-alcohol testing, however, where human subjects are involved, the situation is more complex, as detailed in this article. Certainly, wet or dry gas standards do not mimic the human subjects evaluated by breath-alcohol analyzers. Consequently, the calibration protocol that is in place must necessarily be considered in conjunction with the potential impact of variables, such as those addressed in this article, which can adversely affect the reliability of a particular analytical result.

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Notes

1. It should be noted that truncation is the standard practice in law enforcement for reporting BACs, so that results of breath-alcohol analyses are uniformly reported to two decimal places (9).

2. Personal error, the third type of systematic error (13), is assumed to be minimal when breath-alcohol analysis is properly conducted.

3. See, for example, the description of the breath-alcohol analyzer, Intoxilyzer 5000EN, in the Web site of CMI, Inc., the manufacturer of this instrument: <http://www.alcoholtest.com> (accessed July 2002).

4. This infrared-based breath-alcohol analyzer relies on two analytical wavelengths corresponding to the asymmetric and symmetric stretching vibrations of the methyl group, namely 3.39 μm ($\bar{\nu} \approx 2950 \text{ cm}^{-1}$) and 3.48 μm ($\bar{\nu} \approx 2974 \text{ cm}^{-1}$), respectively.

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