

Possible Causes and Effects

Perhaps the senior scientist, knowing the above, queries the younger team members, who reply "uncorrected" because they have not personally done anything about it and do not realize they are giving the wrong answer.⁷ Others, aware that corrections are very small (at low temperatures!) consider the matter to be unworthy of their attention. Some authors may be confusing "uncalibrated" with "uncorrected". There may also be cases of "conditioned reflex".

What harm results? Fortunately not very much, for the lower melting points suffer little uncertainty, and (if the above analysis is valid) for the higher ones the statement "uncorrected" can be ignored in most cases. The damage, aside from possible embarrassment, lies in creating lingering uncertainty about data that should be definite and above reproach; it is unnecessary.

Recommendations

What can be done? Firstly, informed researchers and authors should determine which statement applies and use it properly. Secondly, journal editors can require that an in-

formed statement be made; for example, rather than naming the apparatus used, the Experimental section of a paper should name the thermometer used.¹¹ Thirdly, since the objective is to determine with maximal accuracy the true melting temperature, journal editors, authors, and researchers should begin to use the term "certified" to indicate claims for accuracy by the manufacturer of an apparatus or thermometer (when known), or preferably the term "calibrated" to signify that a series of high-purity materials of well-established melting points have been run and that any observed discrepancies have been used to prepare a calibration graph or table (rechecked occasionally) from which true temperatures can be determined. Notably, none of the 136 papers surveyed above mentioned calibration of their equipment.

¹¹ For example, the generic term "ASTM 2C" imprinted on the back of a thermometer specifies 76 mm immersion and reading to 300 °C within a prescribed accuracy, regardless of manufacturer.

The Chemical Basis of the Breathalyzer

A Critical Analysis

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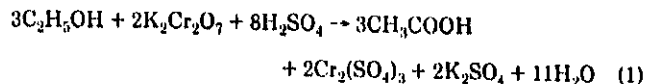
The driver who operates an automobile while under the influence of alcohol is a public menace. The annual toll extracted from society in the United States alone by drivers operating under the influence of alcohol (OUIA)—in terms of ruined and lost lives, property damage, and increased automobile insurance costs for all drivers—is astronomical. There can be no doubt that every effort must be made to prevent the OUIA driver from transforming the automobile into a lethal, or otherwise damaging, weapon. Moreover, educating drivers so that they become, and remain, acutely aware of the dangers and consequences of driving while intoxicated (DWI) must be a part of this effort. Certainly, the noted national organization MADD (*Mothers Against Drunk Driving*) is playing a key role in promoting the public's perception of DWI as a practice to be shunned.

Given the seriousness of the DWI scenario, law enforcement authorities have resorted to strict enforcement of DWI statutes. While many jurisdictions currently utilize physical methods of breath-alcohol analysis to evaluate suspected OUIA drivers, such as infrared spectrophotometry, the Breathalyzer, developed by Borkenstein (1, 2) and based on redox chemistry and Henry's law, remains the tester of choice in many cases. The continued use of the Breathalyzer is perhaps a consequence of its long-standing status in law enforcement circles as a reliable, noninvasive instrument for forensic alcohol analysis (3).

The reliability of the Breathalyzer, however, has been questioned extensively in recent years. This article addresses several of the key chemical issues that are central to the controversy surrounding this classic breath-alcohol tester.

Operational Features

The chemistry of the Breathalyzer is depicted in eq 1 and involves the reduction of potassium dichromate by ethanol contained in the breath sample of a test subject.



The instrument is equipped with two ampules containing yellow solutions of 0.75 mg (25×10^{-7} mol) of $K_2Cr_2O_7$ in 3 mL of 50% H_2SO_4 (v/v), and 0.75 mg (44×10^{-7} mol) of silver nitrate, a catalyst that ensures complete oxidation of ethanol to acetic acid within 1.5 min. One of the ampules is a sealed reference ampule; the other, opened before a suspected OUIA driver is tested, is the one into which the breath sample is delivered. Prior to testing, a photometric balance between light transmitted through the reference and test ampules is established. If subsequent reduction of Cr(VI) to Cr(III) by ethanol occurs, the intensity of the yellow color of the test solution decreases, and the photometric balance must be reestablished. The extent to which the original balance is disturbed is a measure of the reading ultimately obtained on the linear Breathalyzer scale. The scale, calibrated in units of percent blood-alcohol concentration (BAC), covers a range of 0 to 0.40%, weight by volume (w/v). Specifically, the BAC is the number of grams of ethanol per 100 mL of blood, and in most states, a lower limit of 0.10% is the minimum BAC for a DWI conviction.

Blood- to Breath-Alcohol Partition Ratio

A major factor in the calibration of the Breathalyzer is the "2100:1 partition ratio" (4). The ratio states that, at 34 °C, the average temperature of expired alveolar air, 2100 mL of this air contains the same weight of ethanol as 1 mL of blood. Alternatively, each milliliter of blood has 2100 times the weight of ethanol as each milliliter of alveolar air. This ratio is the reciprocal of the partition coefficient $K_{A/B}$ (5), which reflects the equilibrium distribution of ethanol between alveolar air (A) and circulating pulmonary blood (B) at a given temperature, in accord with Henry's law.

The sample of breath trapped by the Breathalyzer has a volume of 52.5 mL and is considered alveolar because it is the last portion of a prolonged expiration (6). The analysis of the sample automatically includes multiplication by a factor of 40 to convert the number of grams of ethanol in the 52.5 mL sample to the number in 2100 mL of alveolar air (or 1 mL of blood), and by a factor of 100 to provide the number of grams of ethanol in 100 mL of blood and, hence, the BAC (eq 2):

$$\% \text{ BAC} = \frac{\text{g Ethanol}}{52.5 \text{ mL Breath}} \times \frac{2100 \text{ mL Breath}}{1 \text{ mL Blood}} \times 100 \quad (2)$$

A BAC reading so obtained reflects, in reality, the oxidation of only a trace quantity of ethanol. For example, a 0.10% BAC is indicative of the analysis of 25 μg of ethanol. Moreover, the stoichiometric relationship between any recorded BAC and the corresponding trace mole quantity of $\text{K}_2\text{Cr}_2\text{O}_7$ reduced according to eq 1 is depicted in eq 3:

$$\begin{aligned} \text{No. mol } \text{K}_2\text{Cr}_2\text{O}_7 \text{ reduced} &\times \frac{3 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{2 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \times \frac{46 \text{ g } \text{C}_2\text{H}_5\text{OH}}{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}} \\ &\times \frac{2100 \text{ mL Breath}}{1 \text{ mL Blood}} \times \frac{1}{52.5 \text{ mL Breath}} \times 100 = \% \text{ BAC} \quad (3) \end{aligned}$$

Deviations from the 2100:1 Partition Ratio

Interestingly, the 2100:1 partition ratio is a compromise value derived from numerous studies. Generally cited upper and lower limits range from about 1100:1 to over 3000:1 (7-10), although Breathalyzer experts Mason and Dubowski (7) have said that, if there is a true ratio, it probably lies somewhere in the range of 1900 to 2400:1. In fact, Dubowski and O'Neill (11) reported a mean ratio of 2280:1. This was based on their analyses of 397 paired breath and blood specimens obtained simultaneously from healthy adult males, with a range of 1555:1 to 3005:1 estimated for 99.7% of their test population (12).

Nevertheless, the possibility of an OUIA driver having a partition ratio significantly different from 2100:1 cannot be discounted, and in such a case, justice would not be served. If, for example, a suspected OUIA driver produced a Breathalyzer reading of 0.10%, and if the driver actually had a 1100:1 ratio, his/her BAC should have been 0.052% (1100/2100 of 0.10%, since the Breathalyzer scale is linear). A similar calculation for a person with a 3200:1 ratio would yield a BAC of 0.15%. Obviously, the Breathalyzer would benefit the OUIA driver having a ratio higher than 2100:1 (a lower than actual BAC would be obtained) and would discriminate against the OUIA driver with a ratio lower than 2100:1 (a higher than actual BAC would be obtained). In effect, the Breathalyzer equalizes all OUIA drivers.

This equalization is questionable and was recently addressed by Fitzgerald and Hume (13). They described a case (State of Nebraska v. Burling) that was decided by the Nebraska Supreme Court in 1987. The defendant had a BAC of 0.164%, which was determined by a particular model of the Intoxilyzer, an instrument based on infrared spectrophotometry and, like the Breathalyzer, utilizing the 2100:1 ratio. The expert witness for the defense, a pharmacologist, testified that this result was unreliable because the blood-to-breath-alcohol ratio is a variable quantity. He cited ratios ranging from 1100:1 to 3400:1. The Court concluded that, if the defendant had had an 1100:1 ratio at the time of testing, his BAC should have been 0.086%, or about 52% of the original BAC. The Court's decision was based on an earlier ruling, State of Nebraska v. Bjornsen (1978), which specified that a defendant is entitled to the benefit of any margin of error associated with a test result.

One of the foremost proponents of breath-alcohol analysis, Kurt Dubowski, whose work was referred to above, has also questioned the validity of a uniform application of the 2100:1 ratio. In testimony that he gave in the case of *Municipality of Anchorage v. Serrano*, Alaska Court of Appeals (1982), he admitted that, since his own research showed 14% of his test subjects to have blood- to breath-alcohol ratios below 2100:1, a safety factor of 0.025% should be subtracted from Breathalyzer readings (14). Although not as substantial a reduction as the one endorsed by the Nebraska Supreme Court, Dubowski's safety factor would, nevertheless, be significant, particularly in borderline cases.

The obvious problem with the concept of the blood- to breath-alcohol ratio prompted Dubowski (11, 15) and Jones (3) to recommend that suspected OUIA drivers be evaluated on the basis of statutorily defined limits of breath-ethanol concentrations. This practice would eliminate the conversion of a suspect's breath-alcohol concentration to a corresponding BAC, and, therefore, the application of the 0.025% safety factor would be unnecessary. Unfortunately, this approach can also be flawed. For example, those states that have set breath-alcohol limits in terms of grams of ethanol per 210 L of breath have, in fact, employed the concept of the 2100:1 partition ratio. Thus, a 0.10% BAC would be the equivalent of 0.10 g of ethanol per 210 L of breath. Consequently, if a breath-alcohol concentration is to be used as a measure of culpability in a DWI case, then it must be correlated with a range of BAC values with which it is consistent (16).

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Temperature Factor

The effect of temperature on $K_{A/B}$, and consequently on the 2100:1 ratio, also affects the accuracy of Breathalyzer testing. As temperature increases, $K_{A/B}$ increases, since, at the higher temperature, more ethanol leaves the blood to enter alveolar air. This produces a decrease in $1/K_{A/B}$ and a corresponding decrease in the 2100:1 ratio. In such a situation, an OUIA driver with a lower blood- to breath-alcohol ratio due to an increase in breath temperature would produce a higher than actual BAC on the breathalyzer. Obviously, the reverse would occur with a decrease in temperature.

Using values of $K_{A/B}$ reported by Harger et al. (17), Legge (5) determined blood- to breath-alcohol ratios as a function of temperature between 33 °C and 37 °C (table). Since the relationship between $K_{A/B}$ and temperature is essentially linear in this range, Legge used eq 4—where K_L and K_H are the blood- to breath-alcohol ratios at lower and higher temperatures, respectively—to predict percentage increases in BAC's due to increases in breath temperature. Thus,

$$\text{Predicted \% Increase} = \frac{K_L - K_H}{K_H} \times 100 \quad (4)$$

between 33 °C and 37 °C, the predicted increase in BAC would average 6.5% per 1 °C rise in breath temperature.

Surprisingly, Legge's observed mean increase in breath-alcohol level per mean increase of about 1 °C in breath temperature was nearly 23%, based on a study of 10 subjects, each of whom consumed the same quantity of an alcoholic beverage. The rather large difference between predicted and observed increases led Legge to conclude that a change in breath temperature is not the only factor effecting a change in breath-alcohol level during an expiration. He cited as contributing factors the differential rates of equilibration at different points in the respiratory tract, the length of time

Blood- to Breath-Alcohol Ratios as a Function of Temperature

Temperature (°C)	Ratio
33	2179:1
34	2057:1
35	1935:1
36	1813:1
37	1692:1

for equilibration to occur, and individual differences in breathing habits.

With regard to the last of these arguments, a study by Jones (18) demonstrated that if subjects hold their breath prior to expiration, thereby allowing more time for equilibrium to be reached between ethanol levels in blood and alveolar air, the concentration of ethanol in expired air could increase by as much as 18%. On the other hand, hyperventilating prior to expiration could reduce ethanol concentrations by as much as 12%.

Despite the fact that Legge's results indicate no simple correlation between increases in breath temperature and corresponding increases in BAC, the temperature factor is an important consideration in Breathalyzer analyses. Hume and Fitzgerald (19) have stressed that the temperature gradient between mouth and lungs is substantial and encompasses the range in which the vapor pressure curve of ethanol rises steeply. Jurisdictions employing breath analysis should thus consider Mason and Dubowski's recommendation (7), that the temperature of breath samples should be determined, and corrections should be made when significant deviations from the norm occur.

Hematocrit Factor

The hematocrit represents the fraction of whole blood composed of red cells and is correlated with the aqueous content of blood. The higher the hematocrit, the lower the concentration of water in blood, and vice versa. The average hematocrit for normal, healthy males is 47%, with a range of 40-54%; for females, the average is 42%, and the range is 36-47% (20).

Since ethanol dissolves almost entirely in the aqueous component of blood (9, 21), two individuals with identical actual BAC's but with different hematocrits would be expected to produce different Breathalyzer results. The person with the higher hematocrit, and therefore lower blood-water content, would necessarily be characterized by a higher concentration of ethanol in the aqueous component of his/her blood and, consequently, by a higher Breathalyzer reading (9).

This point is in accord with the data of Jones (21), who determined partition ratios for dilute solutions of ethanol in water, whole blood, and plasma (whole blood minus cells). At 34 °C, the partition ratio for whole blood (85.0 g H₂O/100 mL blood) was 2143:1; for plasma (94.5 g H₂O/100 mL plasma), 2448:1; and for water, 2587:1. Obviously, as the water concentration decreases, the partition ratio decreases, indicating that, the higher a suspected OUIA driver's hematocrit, the higher the concentration of ethanol in his/her alveolar air. Given that the Breathalyzer uses only one partition ratio, Smith (9) and Payne et al. (22) have predicted that the normal variation in hematocrit can produce errors in breath test results in the 10 to 14% range.

The above analysis relates to the use of the "simulator solution" by Breathalyzer operators to ascertain that the instrument is functioning properly. At 34 °C, this solution of ethanol in water, which contains 0.1226 g of ethanol per 100 mL (0.1226% w/v) (9), produces a reading of 0.10% on the Breathalyzer. In effect, if the simulator solution is assumed to be a human test subject with a partition ratio of 2587:1, based on Jones's data (21), the Breathalyzer, as expected, would benefit the subject by giving a false low result (2100/2587 of 0.1226%).

Conclusion

Although the Breathalyzer has played a significant role in the enforcement of DWI statutes for many years, it is obviously an instrument capable of producing flawed data. Nevertheless, breath-alcohol analysis is expected to remain in place (3). Therefore, improvements in the evaluation of suspected OUIA drivers must constitute a priority consideration for forensic scientists and law enforcement authorities.

If the use of the Breathalyzer continues, then the recommendation of Dubowski (23), that 0.055% should be subtracted from any raw test result, should be uniformly implemented. This adjustment includes both the 0.025% safety factor cited above for results reported in terms of BAC, and an additional 0.03% error factor stemming from a study conducted by Dubowski in which 43% of the Breathalyzer readings that exceeded 0.10% were actually below 0.10%.

If, on the other hand, the Breathalyzer is phased out entirely and replaced, for example, with various instruments based on infrared spectrophotometry, then the question of specificity for ethanol in the presence of potential breath-sample contaminants must be addressed (24-26). In addition, any inference of alcohol-induced impaired driving, stemming from the results of a breath analysis, should be reported within the confidence limits of the analysis involved (16, 27, 28), a recommendation obviously in accord with Dubowski's. Moreover, suspected OUIA drivers should be given the option of choosing between a breath test and a direct blood analysis, with the latter procedure recommended when a breath test result is at or near statutory limits (27).

In the final analysis, improvements such as these will ensure that justice will be better served for all parties concerned.

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