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Sulfuric Acid Concentration in the Catalyzed Breathalyzer Ampules

During the last fifteen years the Breathalyzer has been the most widely used instrument in North America for determining blood alcohol concentrations by means of breath analysis [*1*,*2*]. Of the parameters which may affect the alcohol readings, those related to the composition of the ampule reagent are among the most important. At present the manufacturing specifications used by Scientific Services are, by volume, 50 percent aqueous sulfuric acid, 0.025 percent weight per volume, potassium dichromate, and 0.025 percent weight per volume, silver nitrate [*3*]. The total volume of this solution in the ampules may be 3.00 to 3.07 ml. The inclusion of the silver nitrate as a catalyst is a modification of the original formulation which involved only the potassium dichromate in the aqueous sulfuric acid solution [*4*]. It has been shown that the potassium dichromate concentration may vary between 0.015 percent and 0.035 percent weight per volume, and the sulfuric acid concentration may vary between 16 and 20 normal without loss in accuracy [*5*]. Under these conditions ethanol samples introduced into the ampules at approximately 65 C were oxidized stoichiometrically to acetic acid within 90 s [*1*]. The ethanol is first oxidized to acetaldehyde, a short-lived intermediate, rapidly oxidized to acetic acid. Stronger oxidizing conditions than exist in the ampule are needed to take the oxidation beyond the acetic acid stage [*2*,*6*,*7*]. The equations representing the stoichiometry of this progressive oxidation of ethanol are as follows:

1) $2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O + 6O$
2) $CH_3CH_2OH + O \rightarrow CH_3CHO + H_2O$
3) $CH_3CHO + O \rightarrow CH_3COOH$
4) $CH_3COOH + 4O \rightarrow 2CO_2 + 2H_2O$

Silver nitrate is added to the ampule formulation to catalyze the ethanol oxidation with silver (I) ions to the extent that the reaction will be completed within 90 s, but at a lower, more convenient temperature of less than 40 C. Borkenstein [*4*] determined that the catalyst concentration is not critical to the reproducibility of the determination. It is also apparent that the potassium dichromate concentration over a considerable range is not a critical factor, since consecutive reproducible determinations of ethanol samples may be made with one ampule. One factor whose effect on ethanol determination by catalyzed ampule reagent has not been investigated extensively is the sulfuric acid concentration.

In commercial ampules that contain the catalyst, the sulfuric acid is 18.8–19.6 N. (Specifications actually call for specific gravities between 1.51 and 1.53 for the ampule solution [*3*].) In deciding what limits to set on the acid normality, the kinetics of the

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oxidation must be examined. First, the reaction should be complete within 90 s at 34 to 39 C, which is the range of temperature attained by a test ampule in the test ampule well during an analysis. (Ninety seconds was chosen originally as a convenient reaction period, and any alteration in that time period would necessitate procedural modifications.) Since the rate of the oxidation is considerably more sensitive to sulfuric acid concentration than to that of other ampule constituents, the lower limit to the ampule acid normality is determined by the 90-s reaction requirement. Kinetic considerations are also involved in the setting of an upper limit to the acid normality, since the final oxidation product at a certain acid normality may oxidize faster at a higher acid concentration. The thermodynamics of the oxidation are unimportant since all stages of the ethanol oxidation are virtually irreversible under Breathalyzer oxidation conditions. It will be apparent, in the discussion below, that thermodynamic considerations are important, however, as they relate to the reversible polymerization of the ionic species $(CrO_4)^{=}$ in acid media. In this regard the color of the solution is affected and not the oxidation itself. The relevant factor in the oxidation process is the rate at which each of the intermediate oxidation products are converted to the next.

The object of this study was, therefore, to determine, for catalyzed ampule reagent, the range of acid normalities which produced a) oxidation within 90 s at 34 to 39 C, and b) stoichiometric conversion of ethanol to acetic acid.

Experimental Procedure

Apparatus

a) Breathalyzer measurements were made with a Breathalyzer 900 (Stephenson Co.).
b) Simulated breath samples were delivered to the Breathalyzer ampules by means of a Simulator (Stephenson Co.), which delivers air containing an accurately known concentration of ethanol to the Breathalyzer ampule.
c) UV and visible spectrophotometric measurements were made on a Shimadzu, Model MPS-50L, recording spectrophotometer.
d) Volumetric measurements were made with the following apparatus: Kimax Teflon, stoppered 5.00 ml microburettes; Kimax automatic 5.00 ml microburette; and Kimax class A 100λ pipettes.

Reagents

a) Sulfuric acid, Analar or Baker-analyzed.
b) Ethanol (Consolidated Alcohols Ltd.); analyzed by gas chromatography and found to contain approximately 0.1 percent water and less than 0.01 percent of other volatile organics.
c) 1,10-phenanthroline ferrous sulphate complex, Fisher certified.
d) Ferrous ethylene diammonium sulphate, primary standard grade (G. Frederick Smith Chemical Co.).
e) Silver nitrate, Analar.
f) Potassium dichromate, Analar; kept in a desiccator; found to contain less than 10^{-2} percent water.
g) Water. Distilled water was redistilled from sodium hydroxide and potassium permanganate and found to contain less than 10^{-2} ppm of volatile organics.
h) Breathalyzer ampules (The British Drug Houses (Canada) Ltd.); specified to contain 3.00 to 3.07 ml of a solution consisting of silver nitrate (0.025 percent), potassium

dichromate (0.025 percent), aqueous sulfuric acid (50 percent), and having a specific gravity (4 to 20 C) of solution 1.51 to 1.53.

i) Oxidizing solutions, made up of varying sulfuric acid concentrations (measured by pycnometry and titration with sodium hydroxide), while in use were stored in the darkened, 2-l reservoir of a Kimax automatic 5.00 ml microburette.

Nine experimental oxidizing solutions containing 0.025 percent weight per volume of both potassium dichromate and silver nitrate but with sulfuric acid concentrations ranging from 14.9 to 25.1 N were prepared. The solutions were labeled A to H, and J respectively.

Approximately 2 liters of each oxidizing solution were prepared and stored in dark glass bottles.

Methods

All glassware was cleaned with concentrated chromic acid, rinsed thoroughly in distilled water, and finally rinsed several times in double distilled water [6].

Three kinds of measurements were made.

1) Titration—back titration of excess chromic acid following reaction with ethanol, delivered by pipette.
2) Breathalyzer analyses—normal Breathalyzer analyses using commercial ampules and experimental ampules filled with one of the solutions, A to J. Ethanol was delivered by a Simulator.
3) Spectrophotometric transmittance measurements on experimental ampule reagents of various acid concentrations.

The Titration Method.

Calibration of apparatus—Each piece of volumetric apparatus was calibrated by weighing the delivered volumes of the solution that it was to deliver or contain. The calculated volume delivered or contained at a given temperature was converted to the volume delivered at 20.0 C. All of the volumetric apparatus used in these experiments was found to be well within specified tolerances, requiring little or no correction.

Experimental procedure—A dilute aqueous ethanol solution of known ethanol concentration was prepared. A known volume of this solution was pipetted into a flask containing a known volume of one of the experimental solutions. Reaction was allowed to proceed for a fixed time that ranged from 3 to 15 min. Unreacted chromic acid was then back-titrated with standard Oesper's solution (ferrous ethylene diammonium sulphate) using 1,10-phenanthroline ferrous sulphate complex as an indicator. The final volume in the titration flask was always adjusted to make the solution 2 *M* (that is, 4 N) in sulfuric acid by the addition of double distilled water, since the position of the end point depends on pH. Each ethanol oxidation was matched by a blank determination in which double distilled water was pipetted into the chromic acid flask in place of the aqueous ethanol solution.

Oesper's solution was not used as a primary standard, but was standardized by titration with an aqueous potassium dichromate solution. It is believed that the presence of water of crystallization in the Oesper's salt makes it less satisfactory than the dichromate as a primary standard. Potassium dichromate is a well known primary standard in volumetric work [8]. In the standardization of Oesper's solution against potassium dichromate the final titration solution was also made 2 *M* in sulfuric acid by the addition of an appro-

priate volume of 10 N sulfuric acid to the titration flask. Thus the end point occurred at the same hydrogen ion concentration during the standardization as it did during the back titrations. The absolute position of the end point was thus unimportant since the Oesper's solution was, in effect, calibrated by the primary standard aqueous potassium dichromate under conditions identical to those in the actual oxidations. Namely, the volume in the titration flask at the end point was 100 ml; the volume of indicator used was always 2 drops; the concentration of sulfuric acid in the titration flask at the end point was approximately 4 N. This procedure largely eliminated the error introduced by the use of a relatively large volume of indicator. Nevertheless, an indicator blank determination was made, since an accumulation of small errors can assume significance in a multistage analysis. The blank value was determined by titrating Oesper's solution against aqueous potassium dichromate using increasing volumes of indicator. The titer varied linearly with the number of drops of indicator used, enabling an extrapolation to be made to the theoretical titer that would be obtained when no indicator was present.

Following are data from a typical titration: Concentration of aqueous ethanol solution = 1.72×10^{-5} moles/ml. Volume of aqueous ethanol solution added to flask = 0.0892 ml $\equiv$ 1.534×10^{-6} moles. A quantity of 1.534×10^{-6} moles should react with $\frac{2}{3} \times 1.534 \times 10^{-6}$ moles of potassium dichromate = 1.023×10^{-6} moles. Initial volume of experimental solution A in flask = 15.009 ml. After reaction with the 1.534×10^{-6} moles ethanol, titer of Oesper's solution required for the unreacted potassium dichromate = 1.075 ml. (Normality of the Oesper's solution was 0.01214.) A blank determination gave the normality of solution A as 0.00496, therefore, 1.075 ml Oesper's $\equiv$ 2.638 ml of solution A. Hence the volume of A reacted with the ethanol = 12.371 ml $\equiv$ 1.022×10^{-6} moles. Thus, the percentage ethanol conversion to acetic acid was

$$\frac{100 \times 1.022 \times 10^{-6}}{1.023 \times 10^{-6}} = 99.91 \text{ percent.}$$

All volumes were adjusted for a) calibration factors for volumetric apparatus, b) temperature corrections to 20 C, and c) indicator blank corrections. For 2 drops of indicator 0.09 ml were added to the ferrous ethylene diammonium sulphate titer.

Breathalyzer Analyses

Preparation of ampules—Used commercial Breathalyzer ampules were cleaned with concentrated chromic acid, rinsed in double distilled water, and dried. Experimental ampules were then prepared by adding 3.030 $\pm$ 0.005 ml of the solutions, 3 ampules being prepared from each of the solutions. The experimental ampule was placed in the test position in the Breathalyzer. The ampule in the reference side was generally a sealed commercial ampule. Next a simulated breath sample equivalent to 0.150 percent weight per volume alcohol in blood, computed on the basis of a blood breath ethanol ratio of 2100:1, was introduced into the Breathalyzer cylinder from a Simulator solution. This collected sample was then bubbled through the experimental ampule in the normal manner. Instead of merely recording the final reading, however, readings were made at 5, 10, or 15-s intervals until no further increase in transmittance occurred. The first reading was taken immediately following the 30-s bubbling period had ceased. Thus, reaction profiles of Breathalyzer reading against time were constructed for the oxidation of known amounts of ethanol by each of the experimental oxidation solutions A to J. These are illustrated in Fig. 1. As a rule, three ampules representing each experimental solution were tested, three profiles being measured from each ampule. Reaction profiles were also constructed for 30 commercial ampules.

Transmittance Measurements

Measurements were made of the transmittance of: a) sulfuric acid of various normalities; and, b) experimental Breathalyzer reagent of constant potassium dichromate concentration but varying sulfuric acid normality.

Results

Table 1 shows the extent of the conversion of ethanol to acetic acid as a function of sulfuric acid normality in the experimental oxidizing solutions.

TABLE 1—*Stoichiometry of ethanol oxidation by catalyzed Breathalyzer reagent as a function of sulfuric acid normality.*[a]

Experimental Solution	Sulfuric Acid Normality	Oxidation Conditions	Percent Conversion	Mean
A	14.9	20 min. at 50°C	98.7	98.6
			98.6	
			98.6	
			98.5	
			98.7	
			98.3	
B	15.7	3 min. at 50°C	85.5	
		15 min. at 50°C	100.1	100.1
C	16.6	3 min. at 50°C	96.3	96.3
D	18.5	3 min. at 50°C	97.8	97.8
		15 min. at 50°C	101.9	101.9
E	19.4	3 min. at 50°C	99.3	99.3
F	20.5	3 min. at 50°C	101.3	101.3
G	21.4	15 min. at 50°C	103.8	
			103.1	
			103.2	
			102.8	103.2
H	21.6	15 min. at 50°C	100.6	100.9
			100.6	
			101.2	
			101.2	
			101.2	
			100.6	
J	25.1	15 min. at 50°C	102.6	102.5
			102.2	
			102.9	
			102.2	
			102.9	
			102.4	

[a] For data regarding acid normality and temperature employed in 20 dichromate-sulfuric oxidation procedures for determination of ethanol see a summary by R. M. Harger in *Toxicology, Mechanisms and Analytical Methods*, C. P. Stewart and A. Stolman, Eds., Vol. II, Academic Press, 1961, pp. 122–124.

One hundred percent conversion represents stoichiometric oxidation of the ethanol to acetic acid according to the equation:

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3CH_3CH_2OH \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O + 3CH_3COOH.$$

Table 2 presents the results of Breathalyzer analyses with simulated breath, using ampules filled with the various esperimental solutions A to J. Although simulated breath

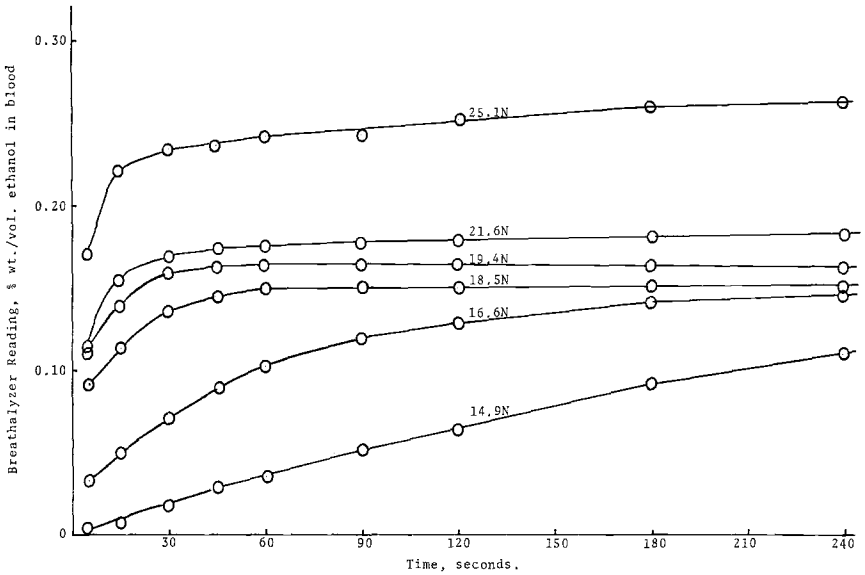


FIG. 1—*Breathalyzer reaction profiles for experimental ampule reagents of different acid normalities.*

samples equivalent to 0.150 percent weight per volume alcohol in blood were delivered, the particular Breathalyzer 900 unit that was used was calibrated to give a reading of 0.142 percent at a 0.150 percent blood alcohol concentration. Thus, 20 analyses with commercial ampules gave an average reading of 0.142 percent blood alcohol. This reading, together with all values obtained for the experimental ampules were normalized to the 0.150 percent concentration by multiplying by the factor 0.150/0.142. Also, while reaction profiles were recorded for each run, only the highest Breathalyzer readings attained during each run are recorded in Table 2 rather than the readings obtained solely after a 90-s waiting period.

Finally, in Table 2 the column heading "Time in seconds to reach 95% of Maximum" means the time taken to reach 95 percent of the highest Breathalyzer reading after the cessation of the 30-s bubbling period. The time to reach 95 percent of the maximum can be estimated with greater accuracy than the time for 100 percent reaction. This is somewhat analogous to the use of half-lives in exponential decay processes where the half-life is attained in a finite time whereas the "whole-life" is theoretically never reached. The 95 percent level was specifically chosen for the reason that the final reading normally taken by a Breathalyzer operator generally lies between 95 and 100 percent of the true maximum.

In Fig. 1 reaction profiles of Breathalyzer reading against time are plotted for 6 experimental ampules filled respectively with experimental solutions A, C, D, E, H, and J. Simulated breath at a 0.150 percent weight per volume blood alcohol concentration was delivered and the readings were normalized as described above. Zero time was taken at the end of the 30-s bubbling period.

Table 3A shows the transmittance of aqueous sulfuric acid solutions at 420 nm as a function of acid normality. (The blue Breathalyzer filters exhibited maximum transmittance at this wavelength.) Table 3B shows transmittance of aqueous potassium dichromate/silver nitrate/sulfuric acid solutions at 420 nm, also as a function of acid normality.

TABLE 2—*Breathalyzer runs with experimental ampules: maximum readings attained and time to attain 95% of the maximum reading, both as functions of sulfuric acid normality.*

Experimental Solution	Sulfuric Acid Normality	Ampule Number	Run Number	Normalized Maximum Breathalyzer Reading, % (wt./vol.)	Mean	Time to Reach 95% of Maximum, s
A	14.9	1	1	0.149	0.148	270
			2	0.148		
			3	0.148		
B	15.7	1	1	0.162	0.150	210
			2	0.157		
			3	0.157		
		2	1	0.153		
			2	0.145		
			3	0.145		
		3	1	0.150		
			2	0.149		
			3	0.142		
C	16.6	1	1	0.148	0.145	140
			2	0.150		
			3	0.141		
		2	1	0.148		
			2	0.142		
			3	0.145		
		3	1	0.145		
			2	0.147		
			3	0.141		
D	18.5	1	1	0.163	0.148	60
			2	0.150		
			3	0.148		
		2	1	0.148		
			2	0.145		
			3	0.147		
		3	1	0.148		
			2	0.145		
			3	0.144		
E	19.4	1	1	0.166	0.159	40
			2	0.162		
			3	0.168		
		2	1	0.158		
			2	0.159		
			3	0.165		
		3	1	0.152		
			2	0.156		
			3	0.150		
F	20.5	1	1	0.174	0.173	30
			2	0.173		
			3	0.168		
		2	1	0.171		
			2	0.176		
			3	0.181		
		3	1	0.168		
			2	0.171		
			3	0.169		
G	21.4	1	1	0.208	0.192	25
			2	0.197		
			3	0.197		
		2	1	0.181		
			2	0.187		
			3	0.197		
		3	1	0.189		
			2	0.183		
			3	0.183		

(*Continued*)

TABLE 2—Continued.

Experimental Solution	Sulfuric Acid Normality	Ampule Number	Run Number	Normalized Maximum Breathalyzer Reading, % (wt./vol.)	Mean	Time to Reach 95% of Maximum, s
H	21.6	1	1	0.181	0.185	25
			2	0.187		
			3	0.187		
J	25.1	1	1	0.246	0.238	25
			2	0.232		
		2	1	0.246		
			2	0.234		

TABLE 3—A) *Transmittance of aqueous sulfuric acid solutions and* B) *of aqueous potassium dichromate/silver nitrate/sulfuric acid solutions at 420 nm as a function of acid normality.*

Sulfuric Acid Normality	% Transmittance
A	
15	92.5
20	92.5
26	92.3
B	
15	52.7
20	48.3
26	19.0

Discussion

The data in Table 1 show that the conversion of ethanol to acetic acid by catalyzed Breathalyzer reagent is essentially quantitative and virtually independent of sulfuric acid normality in the range 15 to 25 normal. This conclusion was supported by experiments carried out with acetic acid, where a negligible amount of oxidation was brought about by experimental solutions.

Why then is the maximum Breathalyzer reading dependent on sulfuric acid normality? The answer almost certainly lies in the dependence of the color intensity of potassium dichromate solutions on pH, especially in concentrated acid media. Table 3 shows quite clearly the reduced light transmittance at 420 nm caused by an increased sulfuric acid concentration in an aqueous solution of potassium dichromate. Silver nitrate does not absorb at 420 nm and is, therefore, noninterfering. This was confirmed by Breathalyzer analyses with experimental, uncatalyzed ampule reagent, which showed the same dependence of Breathalyzer reading on sulfuric acid concentrations.

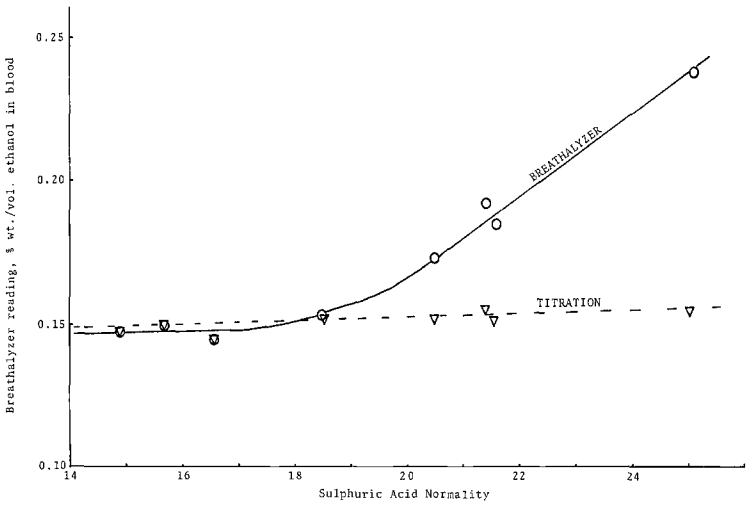
This color intensification that occurs at higher pH values is related to an increased tendency of the hydrolyzed chromium (VI) ion $(CrO_4)^=$ to polymerize under acidic conditions [*9,10*]. Thus, in neutral media Cr^{VI} is hydrolysed to the yellow species $(CrO_4)^=$. In acid solution $(CrO_4)^=$ dimerises to form the orange $(Cr_2O_7)^=$ ion. As the acidity increases the polymerization continues. Three and eventually four $(CrO_4)^=$ monomers condense to form $(Cr_3O_{10})^=$ and $(Cr_4O_{13})^=$ respectively, with an attendant deepening of the orange color that had developed originally in the monomeric $(CrO_4)^=$ itself.

Typical of complex ions of transition metals, the underlying principles of this type of color change are well established [*9,10*]. The color of transition metal ions such as Cr^{VI} is due to *d* electron transitions between two energy levels, resulting in an absorption of electromagnetic radiation in the visible region of the spectrum. When a ligand approaches a transition metal ion and changes its electronic environment, the ion's color is frequently altered. Thus $(CrO_4)^{=}$ is yellow, but the change in the environment of the Cr^{VI} ion that occurs when two of the tetrahedral species combine to form $(Cr_2O_7)^{=}$ moves the *d* electron energy levels closer together, and the dimeric ion is orange. When more ligands approach the Cr^{VI} ion, as further polymerization to trimer and tetramer occurs, the energy levels move still closer together. In the Breathalyzer ampule this results in a shift in the absorption of light by the dichromate solution towards the 420 nm region and produces a more intense color at that wavelength. The blue filter used in the Breathalyzer was found to transmit a narrow band of wavelengths whose maximum transmittance was 420 nm. Clear evidence was also found of the absorption shift to longer wavelengths that occurred with increasing sulfuric acid concentration.

Another way of looking at this color intensity variation is to consider the fundamental equation of spectrophotometry,

$$A = \log I_0/I_x = \epsilon lc$$

where I_0 and I_x are the intensities of incident and transmitted light respectively, A is absorbance, l is the cell path length, c is the concentration of potassium dichromate in the Breathalyzer reagent and ϵ is the molar extinction coefficient. A plot of A against sulfuric acid concentration of Breathalyzer reagent, with constant l and c, is equivalent to a plot of ϵ against the sulfuric acid concentration. Figure 2 is just such a plot, since the Breathalyzer reading is an absorbance measurement, and it is apparent that, past the 17–18 N sulfuric acid region, ϵ increases as acid concentration increases.



○ Variation of maximum Breathalyzer reading.
▽ Variation of corresponding titration values.

FIG. 2—*Effect of variations in sulfuric acid normality on maximum Breathalyzer readings.*

Influence of H_2SO_4 Normality on Breathalyzer Reading

The effect that variations in sulfuric acid normality have on maximum Breathalyzer readings, without regard to a 90-s waiting period, is taken from the data of Table 2 and shown in Fig. 2. The normality of the sulfuric acid used in a given ampule is plotted against the Breathalyzer reading obtained for simulated breath samples equivalent to 0.150 percent weight per volume alcohol in blood. At lower normalities, for example, less than 17–18N, the maximum Breathalyzer readings produce the initial flat portion of the curve with values close to 0.150 percent. When the acid normality reaches 18, however, the curve starts to rise sharply until at 25N the maximum Breathlyzer reading has reached 0.236 percent weight per volume and continues to increase.

The broken line in Fig. 2, representing the stoichiometric data obtained by titration, shows that the amount of dichromate (159 μg) required to oxidize 37.5 μg of ethanol (equivalent to a sample of simulated breath at the 0.150 percent weight per volume blood alcohol concentration) is virtually independent of sulfuric acid normality. However, since the color intensity of the dichromate solution becomes strongly dependent on sulfuric acid concentration at approximately 17–18N, the reduction of 159 μg of dichromate is accompanied by a larger and larger color loss, the higher the acid normality rises beyond the critical value. In other words, a Breathalyzer that is calibrated using ampules whose acid normality is 17–18N, or less, will read high with ampules whose concentration exceeds 18N.

It is interesting to note that the unique system of checks that is built into the Breathalyzer and its operation enables the operator to diagnose the possible presence of an abnormally high sulfuric acid concentration in a given ampule. When a fresh ampule is tested with a Simulator solution at the 0.150 percent blood alcohol concentration the Breathalyzer reading will be higher than 0.150 percent if the acid normality is too high. The operator will simply reject the ampule if the reading exceeds the expected value by more than 0.01 percent weight per volume which is the maximum tolerance permitted.

The lower limit that is set on the acid normality will influence the choice of an upper limit. From Fig. 2 it can be demonstrated that 18.0 is a critical value for the acid normality. The curve shows that at 18.0 N, 95 percent of the reaction is complete in 75 s. Generally, a further 3 to 4 percent reaction occurs within the next 10 to 15 s. Thus 98 to 99 percent reaction has occurred by 85 to 90 s. (In practice a Breathalyzer operator will wait a full 90 seconds before starting to make his measurement. He will actually take his reading at the 100 to 115 s mark.) At an acid normality of 16.0, 95 percent reaction is complete in 180 s, while at the 20.0 N level, 95 percent reacton has occurred after 35 s.

From the kinetic point of view, acid normalities of less than 18.0 are too low. Ninety-five percent reaction should occur within 75 s and sulfuric acid normalities of greater than 18.0 N are required to achieve this.

In Fig. 2 the Breathalyzer reading obtained with 18.0 N acid is 0.148 percent weight per volume blood alcohol. As the acid concentration increases past 18.0 N the Breathalyzer reading increases. At 19.0 N the reading is 0.153 percent, an increase of 0.005 percent over the 18.0 N value, or close to the maximum variation that can be tolerated from a single source of error. This implies that a lower limit of 18.0 N, set by kinetic considerations, is accompanied by an upper limit of 19.0 N, determined by the increasing color intensity of the ampule reagent with increase in acid concentration.

From the color viewpoint it would be preferable to work on the flat part of the curve in Fig. 2, that is, below 18.0 N, where color intensity is not a function of pH (that is, at a constant molar extinction coefficient). Unfortunately, as already pointed out, the reaction is too slow in this region, thus forcing the use of the curved portion beyond 18.0 N. Here,

the gradient of the curve determines just how wide a range of normalities will be acceptable. Bearing in mind that the lower limit can be set anywhere beyond 18.0 N, consider the effect of choosing a lower limit of 20 N. At 20 N, Fig. 2 shows a Breathalyzer reading of 0.166 percent weight per volume. A reading of 0.171 percent is obtained at 20.3 N. Thus the choice of a lower limit of 20.0 N also fixes the upper limit at 20.3 N and allows a range of only 0.3 N for the sulfuric acid concentration. Considering only normalities of greater than 18.0, the gradient of the curve is minimum at 18.0 N. Thus from the foregoing considerations, the optimum limits are 18.0 N (lower) and 19.0 N (upper), where the time factor can be satisfied along with the greatest tolerable range in sulfuric acid concentrations. The 18.5 N Breathalyzer reaction profile in Fig. 1 illustrates the desirable features possessed by a curve obtained from an ampule whose acid concentration lies well within the limits of 18.0–19.0 N.

The Breathalyzer reading is 0.150 percent weight per volume for a 0.150 percent Simulator solution. The reaction is virtually over in 60 s. No further reaction occurs after 60 to 70 s. At higher acid normalities, for example, 21.4 N and 25.1 N, a slight tendency to further reaction is apparent, since the curves continue to rise even after 3 to 4 min.

Conclusion

Present specifications for commercial ampules allow a specific gravity range of 1.51 to 1.53 for the ampule reagent, equivalent to a sulfuric acid normality range of 18.8 to 19.6.

The results of the present study indicate that if the lower limit is set at 18.8 N, then the upper limit will be approximately 19.5 N, allowing for an increased reading of 0.005 percent weight per volume. Thus, while the results presented indicate that 18.0 to 19.0 N represents the greatest acceptable range for the ampule acid normality, consistent with practical Breathalyzer usage, the currently employed range of 18.8 to 19.6 N is also fully consistent with the results that were obtained. However, the acceptable acid normality range is thereby slightly narrowed. The use of a lower acid normality limit of 20.0 N or greater would, in turn, require considerably more rigid and narrower normality specifications. The instruments must, of course, be calibrated in accordance with the acid specifications employed.

Acknowledgments

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