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On the Choice of Color Filters for the Breathalyzer®

In a previous publication [*1*] the authors discussed the influence exhibited by the sulfuric acid concentration in catalyzed Breathalyzer® ampules, considering fundamental principles. This publication serves as an extension to that work wherein the influence of the colored filters chosen for use in the Breathalyzer® is investigated, again from an examination of fundamental principles.

It is of importance that the basic principles are understood well by the scientific personnel responsible for providing the laboratory support services for a breath test program. In our experience the expert who interprets breath test readings in court is often required to elucidate the finer points of Breathalyzer® operation. Not only the working but the theory of each component part of the instrument is open for discussion, particularly in cross-examination. Moreover, it is felt that the chemists who provide the laboratory support service should, nevertheless, have a clear idea concerning the parameters affecting Breathalyzer® readings. The article has been written with this in mind.

The reagents, apparatus, and methods have been described in the previous publication [*1*].

When a reading is made the Breathalyzer® passes filtered light from a tungsten lamp through the ampule solution[2] [*2*]. Ethanol contained in a fixed volume of a person's deep lung breath, delivered to the ampule, reduces some of the dichromate in the ampule solution and the attendant loss in color allows more light to pass through the solution. This increased light transmittance is measured by a selenium photovoltaic cell of the barrier layer type [*5*].

The Breathalyzer's® tungsten lamp source and selenium detector are chosen, presumably, for their low cost and portability. Figure 1, Curve A, shows the relative energy distribution of a typical tungsten lamp as a function of wavelength [*5*]. Figure 1, Curve B, shows the spectral response of a typical selenium barrier layer cell [*5*]. The Breathalyzer® combines a tungsten lamp and a selenium detector and Fig. 1, Curve C, shows the spectral response of a Breathalyzer® selenium detector to monochromated tungsten light scanned from 350–650 nm. The data in Fig. 1, Curve C, were obtained by passing light from a tungsten lamp through a monochrometer onto the surface of a selenium detector taken from a Breathalyzer® 900. The detector leads were attached to a millivolt recorder and the wavelength range from 350–650 nm was scanned manually.

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[2] For the purpose of this discussion it may be assumed that an ampule solution is 0.025 percent (weight/volume) in $K_2Cr_2O_7$ and also in $AgNO_3$ [*3,4*], varying only in H_2SO_4 concentration, which will be specified. Thus, the above solution may, for instance, be referred to as "a 19 *N* ampule solution." An ampule solution that is 22 *N* in H_2SO_4 will be referred to as "a 22 *N* ampule solution," and so on.

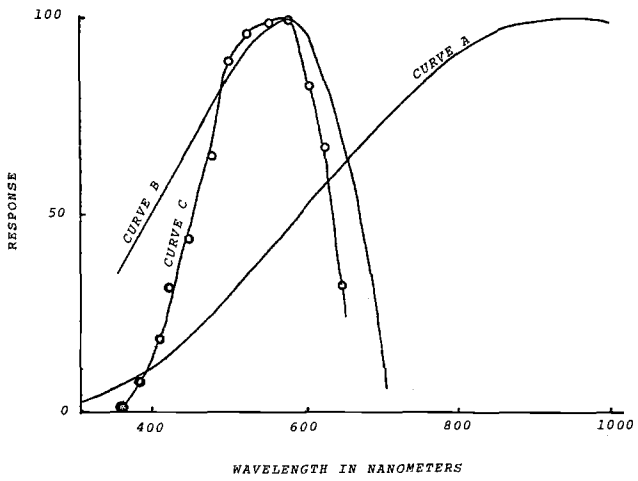

FIG. 1—*Curve A, relative spectral energy output of a tungsten lamp at 2870 K; Curve B, relative spectral response of a typical barrier layer cell; and Curve C, characteristic of a tungsten lamp as measured by a selenium barrier layer cell of the type used in the Breathalyzer® 900.*

It should be stressed that the Breathalyzer® has no monochrometer and that, in the absence of a filter, all of the tungsten light that falls within the detection limits of the selenium photocell will be detected by the photocell. To understand why a blue filter is needed in the Breathalyzer® the absorbance pattern of the ampule solution must be considered. The fact that this absorbance pattern varies noticeably with changes in sulfuric acid concentration is evident from Fig. 2. It consists of absorbance curves between 340 and 740 nm for six ampule solutions whose acid normalities varied from 14 to 25 *N*. The data in Figs. 2 and 3 were obtained on a Shimadzu ratio recording spectrophotometer. The effect of introducing a fixed amount of ethanol into an 18 *N* ampule solution is shown in Fig. 3. There is a marked increase in transmittance for the reacted solution, as compared with the unreacted solution, at wavelengths below about 480 nm.

One is thus confined to the region 400–480 nm for two quite different reasons. In the first place, at wavelengths below 400 nm, not only is very little light emitted by the tungsten lamp but what little light exists is poorly detected by the selenium detector (Fig. 1, Curves A, B, and C). This was confirmed in the Breathalyzer® 900 by using a matched pair of filters that gave a maximum detector response at approximately 400 nm. Very little signal was obtained from the Breathalyzer's® selenium detector. Secondly, with respect to the upper wavelength limit, the reacted and unreacted absorbance curves for an 18 *N* ampule solution, Fig. 3, show that ΔA, the change in absorbance, for a given reduction of dichromate, approaches zero rapidly at wavelengths much above 480 nm. Again, this was confirmed in the Breathalyzer® 900 by the use of a matched pair of filters, this time with a maximum detector response at approximately 515 nm.

An examination of Fig. 3 suggests that any region within the range from 400–480 nm could be used for absorbance measurements. The curves in Fig. 3 were obtained with an 18 *N* ampule solution in the sample side of the recording spectrophotometer while the reference cell contained 18 *N* sulfuric acid only. The upper curve was produced before reaction with ethanol while the lower curve was produced following the addition of 10.0 μl of ethanol to the sample cell and consequent oxidation of the ethanol. The change in

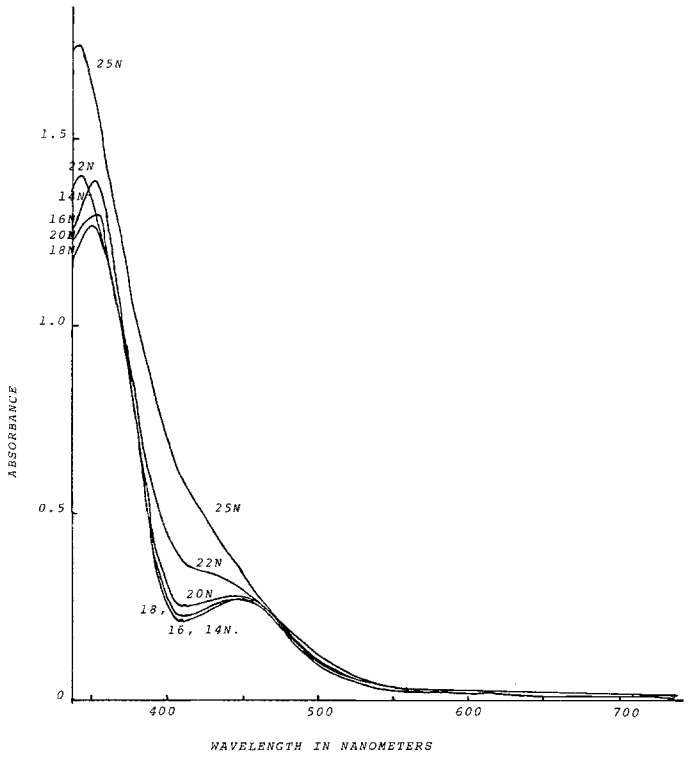

FIG. 2—*Absorbance curves for ampule solutions of various acid normalities.*

absorbance, ΔA, is sufficiently large and also reasonably constant between 400 and 480 nm. One is then confined to the blue region of the spectrum in measuring Breathalyzer® ampule solution absorbance changes for tungsten light detected by a selenium photocell.

The Breathalyzer® 900 uses a filter which for the purpose of this paper will be referred to as the "Type A" filter. Its maximum transmittance of equal energy light as recorded by a ratio recording spectrophotometer occurs at about 420 nm (Fig. 4). Equal energy light is light of which the intensity is independent of its wavelength. Many double-beam spectrophotometers use a slit program which compensates for the spectral energy profile of the light source, thus producing constant energy light. Many spectrophotometers also record the absorbance as a ratio of sample to reference signals. In the Breathalyzer®, however, the tungsten lamp does not produce equal energy light, nor is the detector signal measured as the ratio of its reference signal. Instead, it is dependent on the spectral output of the lamp (Fig. 1, Curve A) and of the spectral response of the selenium detector (Fig. 1, Curve B). The combined effect of measuring the tungsten lamp output by means of the selenium photocell is shown in Fig. 1, Curve C. From Fig. 4 it will be noted that the Type A filter used in the Breathalyzer® 900, whose wavelength of maximum transmittance for equal energy light is 420 nm, will produce a Breathalyzer® photocell response maximum for tungsten light at a higher wavelength of approximately 450 nm, due to the greater abundance of light produced at 450 nm as compared to 420 nm and the greater sensitivity of the photocell at higher wavelengths (Fig. 1). This spectral response characteristic, clearly evidenced in Fig. 4, Curve B, was again recorded by directing mono-

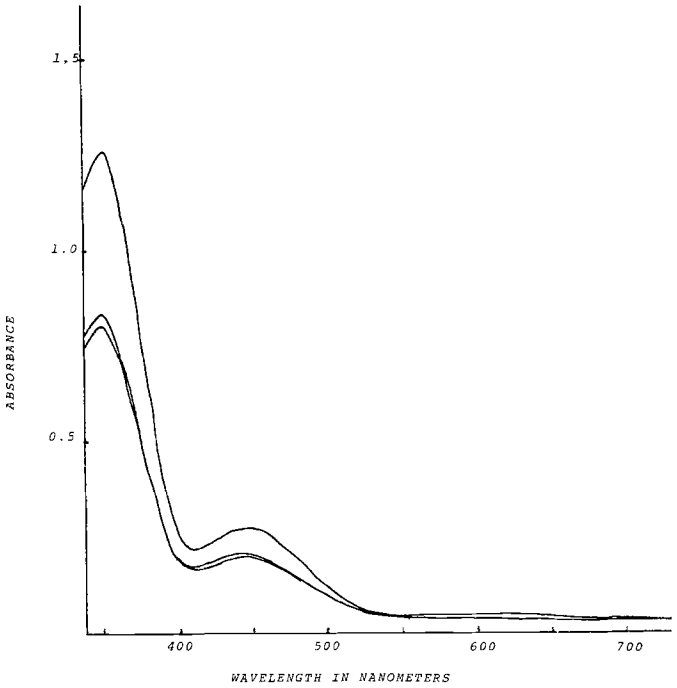

FIG. 3—*Absorbance of an 18* N *ampule solution before reaction with ethanol (upper curve) and after reaction with ethanol (lower curve).*

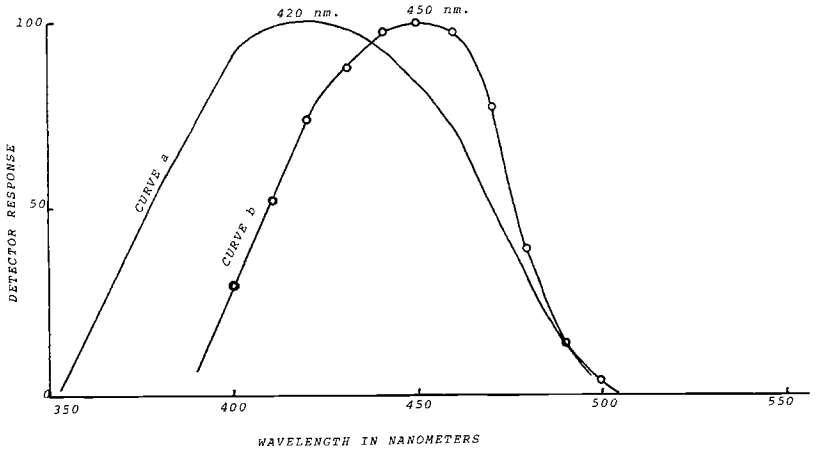

FIG. 4—*Transmittance by Type A filter of (Curve A) equal energy light measured by ratio recording spectrophotometer and (Curve B) tungsten light measured by Breathalyzer's® selenium photocell detector.*

chromated tungsten light through a Type A filter to the photocell and measuring the recorder signal as a function of wavelength. Figure 5 is a schematic diagram of this arrangement.

Figure 6, Curve A, is a spectrophotometer transmittance curve for a filter which will be described here as a "Type B" filter, a type used in the older Model 800 Breathalyzer®.

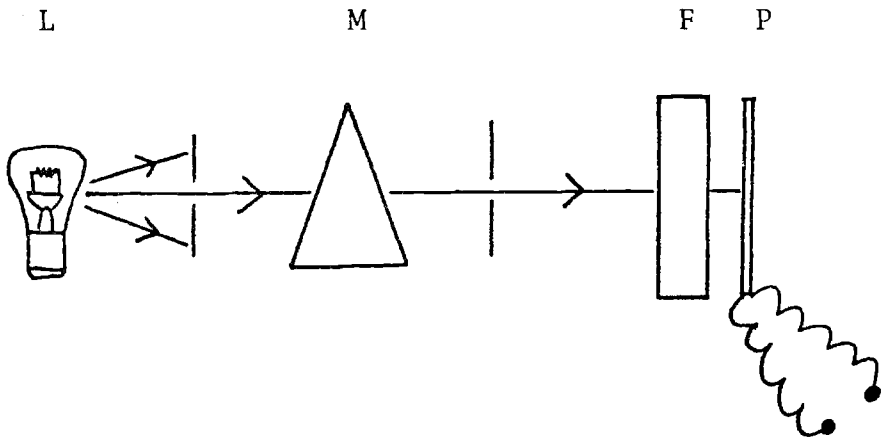

FIG. 5—*Schematic of optics in experimental measurement of selenium photocell* (P) *response to tungsten light* (L = *lamp*) *filtered through various optical filters* (M = *monochrometer*, F = *filter*).

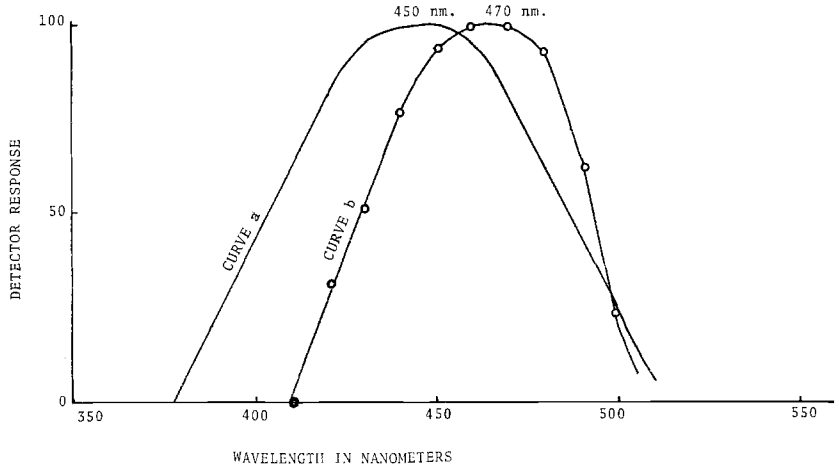

FIG. 6—*Transmittance by Type B filter of* (*Curve A*) *equal energy light measured by ratio recording spectrophotometer and* (*Curve B*) *tungsten light measured by Breathalyzer's® selenium photocell detector.*

The maximum transmittance, as measured with equal energy light by a ratio recorded signal, was approximately 445 nm. Figure 6, Curve B, on the other hand, shows the spectral response of the Breathalyzer® selenium detector to monochromated tungsten light filtered with the same Type B filter, wherein the maximum detector response was at 47 nm. Figure 7, Curves A and B, are corresponding curves for a longer wavelength filter, which for convenience may be called a "Type C" filter that was also used in this work.

Choice of Blue Filter For the Breathalyzer®

To ascertain which part of the blue region between 400–480 nm should be chosen, the dependence of the dichromate color change on sulfuric acid concentration becomes the key factor [*1*,*6*]. In commercial ampules the sulfuric acid concentration is kept within the

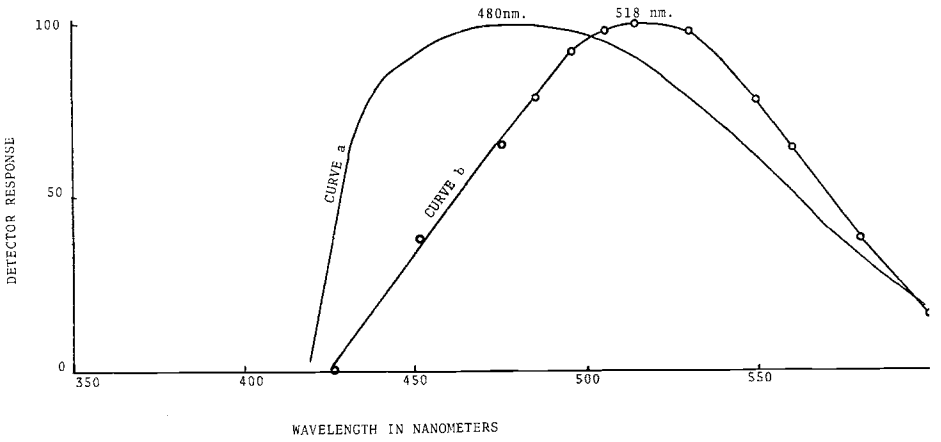

FIG. 7—*Transmittance by Type C filter of (Curve A) equal energy light measured by ratio recording spectrophotometer and (Curve B) tungsten light measured by Breathalyzer's® selenium photocell detector.*

normality range from 18.8–19.6 *N* [*3*]. However, the effect of variations in sulfuric acid concentration on the color change in the ampule is sufficiently marked [*1*] that the choice of an absorbance region which minimizes this effect is highly desirable.

To keep the dependence of this absorbance change (ΔA) on sulfuric acid concentration to a minimum, the molar extinction coefficient (ϵ) should be virtually independent of acid concentration [*1*]. A word of explanation concerning the molar extinction coefficient is probably in order at this point. The Breathalyzer® reading is an absorbance measurement and since absorbance = ϵlc (where ϵ is the molar extinction, l is the ampule path length, and c is the concentration of dichromate in the ampule solution), the Breathalyzer® reading in unreacted solutions is directly proportional to ϵ, since l and c are constant for any given ampule solution. The change, $\Delta\epsilon$, between, say, a 22 *N* ampule solution and an 18 *N* ampule solution is therefore measured by the difference in Breathalyzer® readings between the two solutions. This is true only if each ampule solution contains the same concentration of potassium dichromate, since c in the expression ϵlc is held constant when $\Delta\epsilon$ measurements are being made. In the Breathalyzer®, in addition to wanting a large ΔA, a minimum $\Delta\epsilon$ is wanted [*1*].

Minimum $\Delta\epsilon$ in the Region from 400–480 nm

The change in molar extinction coefficient, $\Delta\epsilon$, and hence the change in Breathalyzer® reading that takes place in ampule solutions as a result of variation in H_2SO_4 concentration, can be estimated from Fig. 2, which shows the trends in $\Delta\epsilon$ as a function of wavelength. A more detailed measure of $\Delta\epsilon$ as a function of wavelength can be obtained from the following expression:

$\Delta\epsilon$ = (ΔA on addition of x moles ethanol to a 22 *N* ampule solution)

− (ΔA on addition of x moles ethanol to an 18 *N* ampule solution)

at any given wavelength.

The absorbance change, ΔA, for x moles ethanol in an 18 *N* ampule solution was plotted against wavelength in Fig. 3 for the addition of 10.0 μl of ethanol. This plot was repeated for a 22 *N* ampule solution. Figure 8 represents a plot of this $\Delta\epsilon$ against wavelength and confirms that $\Delta\epsilon$ is lower at about 470 nm than at 450 nm or less.

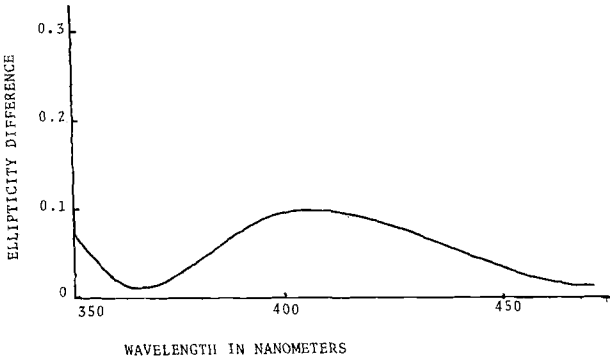

FIG. 8—*Variation of* $\Delta\epsilon$ *(change in ellipticity or molar extinction coefficient) between ampule solutions of 22* N *and 18* N H_2SO_4, *as a function of wavelength.*

It can thus be predicted that a filter giving a maximum Breathalyzer® response around 470 nm will give a Breathalyzer® measurement that is less dependent on H_2SO_4 concentration than a filter producing a maximum response at 450 nm. The Type A filters presently used in many Breathalyzers® produce a maximum response at 450 nm, whereas some older models use Type B filters with a 470-nm maximum detector response (Figs. 6 and 7). Type B filters should show less H_2SO_4 dependence than Type A, and so it was decided to test this hypothesis using the same Breathalyzer® to ensure that other than filter parameters were as constant as possible.

Six ampule solutions of H_2SO_4 normalities 14.82, 16.22, 18.07, 19.07, 21.15, and 23.82, respectively, were used in a Breathalyzer® 900 having a matched pair of Type A filters.

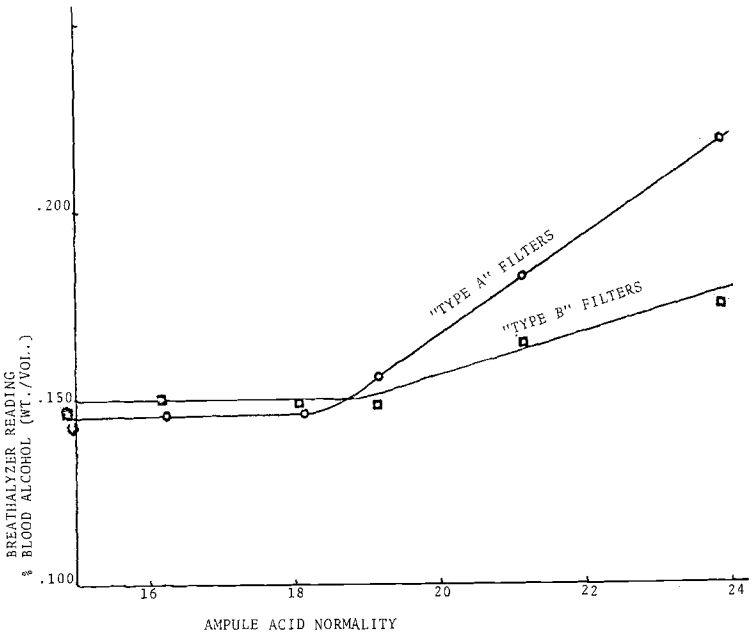

FIG. 9—*Breathalyzer® readings for ampule solutions of six different* H_2SO_4 *normalities using Type A and Type B filters, respectively.*

One reading was obtained from each of six ampules at each normality using a 0.150 percent blood alcohol (weight/volume) simulated breath. This was repeated using Type B filters. However, the Type B filters available were not designed for the Breathalyzer® 900 and in fact, being of higher optical density, they transmitted less light than the Type A filters. It was decided that the simplest way to compensate for the difference in optical density was to use a simulated breath of higher alcohol content with the experimental Type B filters. Consequently, it was found that after substituting Type B filters in the Model 900 Breathalyzer® without recalibration, a 0.190 percent blood alcohol simulated breath produced readings equivalent to 0.150 percent blood alcohol for 18 *N* ampule solutions, which was very close to the results obtained with the 0.150 percent simulated breath with Type A filters in place at this ampule acid normality. This did not affect the validity of the results, since the Breathalyzer® reads linearly up to 0.40 percent blood alcohol (weight/volume) and it was the ratio of the readings, namely, 21 *N* reading to the 18 *N* reading, that was of importance for the purpose of this investigation.

Figure 9 is a plot of: (1) Breathalyzer® reading against H_2SO_4 normality for the Type A filters, and (2) a similar plot for the Type B filters, where each reading has been multiplied by the factor 190/150. Oxidation was allowed to continue to completion (that is, constant reading in each case). It shows quite clearly the decreased acid dependence of the Type B filter readings, which is in agreement with the observed fact that the change in molar extinction coefficient ($\Delta\epsilon$) is smaller at 470 nm than at 450 nm.

Conclusion

In a previous publication in this journal [*1*] it was indicated that the greatest acceptable range of acid normalities was from 18.0 *N* to 19.0 *N*, with 18.0 *N* as an absolute minimum, using a Breathalyzer® containing color filters of the type described here as Type A filters. Furthermore, it was shown that if a lower acid normality limit of 18.8 *N* were chosen (as is at present done in practice) then an upper limit of 19.5 to 19.6 *N* becomes fixed, thereby narrowing the acceptable acid normality range to about 19.2 ± 0.4 *N* sulfuric acid, with appropriately calibrated Breathalyzers®. The work described above dealing with filters has shown that the allowable range with instruments containing the Type A filters, such as the Model 900 Breathalyzers® investigated in this work, could be extended considerably by the use of Type B filters, with maximum Breathalyzer® detector response at about 470 nm. The sensitivity to changes in acid concentration is less pronounced with the use of the latter type of filter (which was used in some older models of the Breathalyzer®) than with the filters found at present in the Model 900.

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