A New Technique For Determining The pH Of Whole Tobacco Smoke

A. J. Sensabaugh, Jr. and R. H. Cundiff
Research Department, R. J. Reynolds Tobacco Company
Winston-Salem, North Carolina, U.S.A.

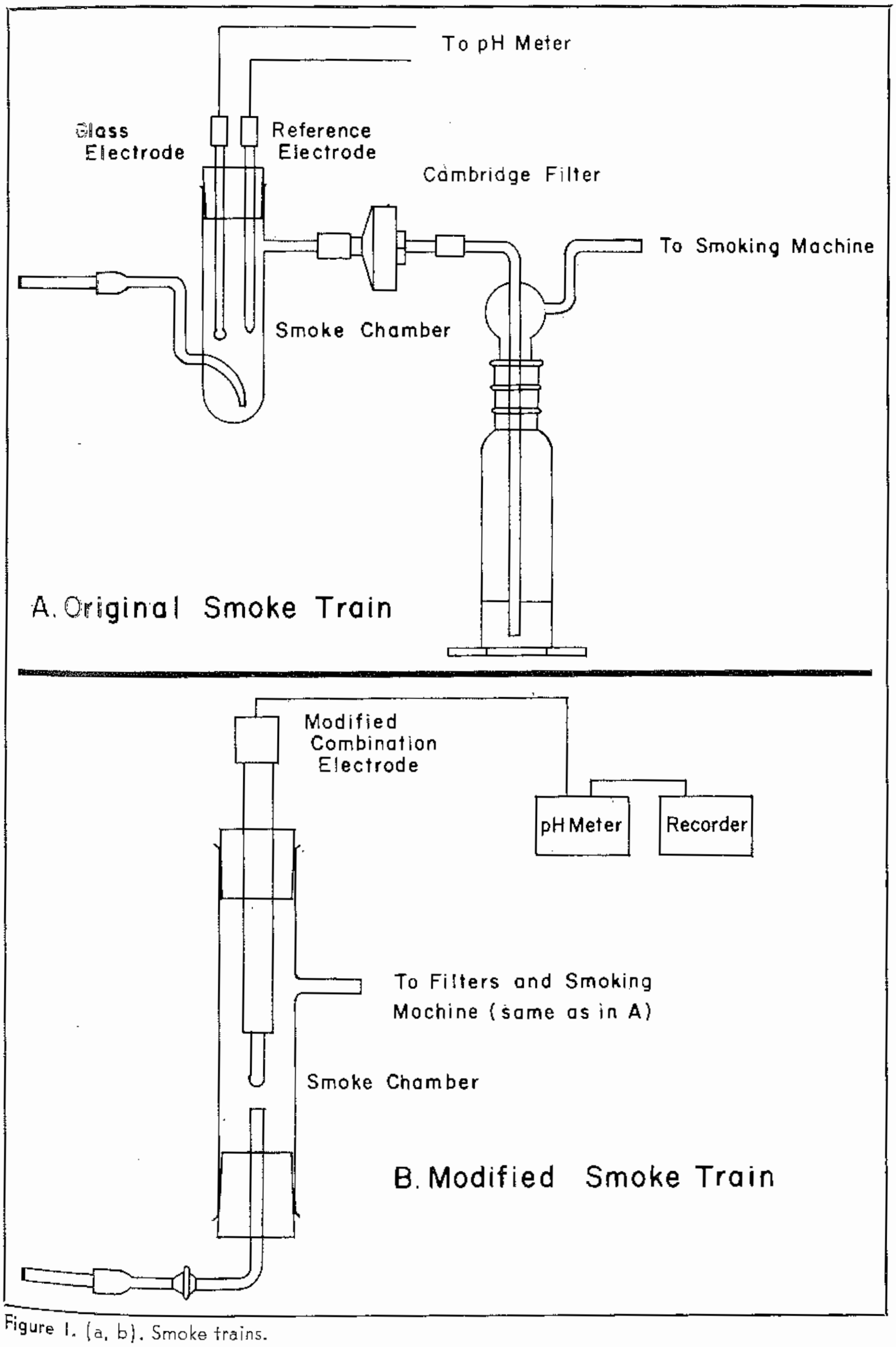

Figure 1. (a, b). Smoke trains.

The efforts to quantitate certain quality factors in cigarette smoke that have been variously described as "bite" or "strongness" have involved the search for comparatively simple tests which would indicate the acidic or basic nature of the smoke. Although the definition of pH would tend to preclude its use in defining an aerosol system, pH-related studies of cigarette smoke have been frequently reported in the literature. Grob (1), for example, described a method for determining the pH and buffering capacity of cigarette smoke using the smoke condensate removed by a cotton filter. Shmuk and Kolesnik (13) reported pH values ranging from 5.6-8.5 from the smoke of various types of tobacco. Kobishi, *et al* (9) listed values for pH of smoke of Turkish, flue-cured, burley, and native Japanese tobaccos. Other workers (10, 12) have published pH values based on a simple performance test of the smoke condensate solution.

In most of these studies, the smoke condensate from several cigarettes was dissolved in water and the pH of the resulting solution determined. The effect of the vapor phase of the smoke was arbitrarily eliminated due to the method of collecting the condensate. Although some acid-base comparisons of smoke may be made by investigating only the condensate from the whole smoke, there is presently no way to properly assess the effect of the gas phase or to correlate the information obtained with the puff-by-puff experiences of the smoker.

Following the precedent established in the prior art, the term "pH of smoke" is used in this study to describe the acid-base effect of whole smoke on an aqueous film under carefully prescribed conditions. This study provides a more rapid and sophisticated approach toward making pH-related measurements of tobacco smoke. The procedure also enables comparison of the pH effect of whole smoke on a puff-by-puff basis.

Effect of Whole Smoke on a pH Indicating System

In preliminary tests whole smoke was passed across a calomel-glass electrode system as shown in **Figure 1A.** After several puffs were taken, a definite pH reading was observed. The reading was reproducible, gave different values for the various types of tobacco, and responded to changes in the acidity or basicity of the smoke. The establishment of a pH reading was presumably due to the formation of a conducing film of smoke condensate across the surface between the glass and calomel electrodes which would establish a potential proportional to the hydrogen ion concentration of the film at the surface of the glass electrode. The pH of the film would depend upon the acid-base balance in the film and the effect of the vapor phase that surrounds it. Kamienski and coworkers (2-8) have published several papers on the detection of acids and bases in nonconducting gas or liquid through the use of a metallic adsorption electrode, coated with silicic acid containing a small amount of quinhydrone. These workers demonstrated that a conducting medium between the reference and indicating electrode had to be established before potential changes were observed. The potential obtained was dependent upon both the thickness and type of medium used. Since the glass electrode is specific for hydrogen ion, the potential established by a film of water between the reference and glass electrodes should be responsive to the passage of an aerosol such as smoke across the film.

Design of Electrode and Smoking Train

The original smoking system shown in **Figure 1A** was subject to random electrical interferences. A more stable system was achieved by substituting a combination electrode for the glass-calomel pair and by making minor changes in the smoke train. The final system consisted of a smoke train, a modified combination electrode, pH meter and recorder arranged as shown in **Figure 1B.** Modification of the electrode involved removing about one inch of the outer glass jacket, replacing the seal with four rubber "0" rings and adding a longer linen thread. Details of the modified electrode are shown in **Figure 2.**

Table 1. pH of Cigarette Smoke

Type of Cigarette	Minimum pH			Maximum pH		
	Mean	Low	High	Mean	Low	High
70 mm. blended, nonfilter	5.80	5.70	5.81	5.98	5.82	6.03
85 mm. blended, nonfilter	5.82	5.77	5.86	6.00	5.91	6.06
85 mm. blended, cellulose acetate filter	5.91	5.85	5.96	6.09	6.04	6.14
85 mm. blended, cellulose acetate-charcoal filter	6.15	6.06	6.25	6.33	6.23	6.40
70 mm. flue-cured, nonfilter	5.70	5.66	5.76	5.84	5.80	5.89
70 mm. burley, nonfilter, uncased	6.62	6.48	6.89	7.14	6.95	7.76
70 mm. burley, nonfilter, cased	6.36	6.28	6.45	6.77	6.65	6.85

Reagents and Apparatus

Smoking Machine. Filamatic Vial Filler, Model AB-5, modified to take a 35-ml. puff of 2 seconds duration once each minute (1).
Smoke Collecting Assembly. Smoke chamber, electrode holder, Cambridge filter assembly, gas washing bottle.
pH Meter. L & N Model No. 7403, or equivalent. The meter preferably should have the expanded scale feature, assignable to any 2 pH range.
Electrode. Beckman Combination Electrode No. 39183, modified as shown in Figure 2.
Recorder. Leeds and Northrup Speedomax W or equivalent.
Buffer Solutions. pH 4, 6, 7 and 10.

Procedure

Assemble the smoke collection assembly and equipment as shown in **Figure 1B.** Set the pH meter on expanded pH range of 5 to 7 and adjust the meter with the pH 7 buffer solution. Check the meter accuracy with the pH 6 buffer solution and return electrode to the pH 7 buffer solution. Remove the electrode from the buffer solution and wipe with tissue to remove excess solution, but do not completely dry the electrode. Place the electrode in the smoking assembly and observe the reading on the pH meter. The pH reading should be between 5.9 and 6.1. If necessary, repeat the above procedure until this specified pH reading is obtained. Place the cigarette to be smoked into the holder and turn on smoking machine and recorder. Light the cigarette as the first puff is taken. Take the desired number of puffs or smoke the desired amount of the cigarette rod. Read the pH values directly from the recorder chart. Remove the electrode from the smoke chamber, wipe with tissue, rinse with water, and place the elec-

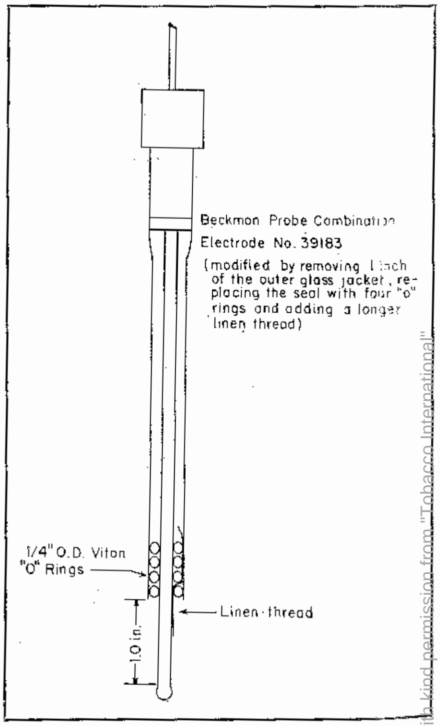

Figure 2. Modified combination electrode.

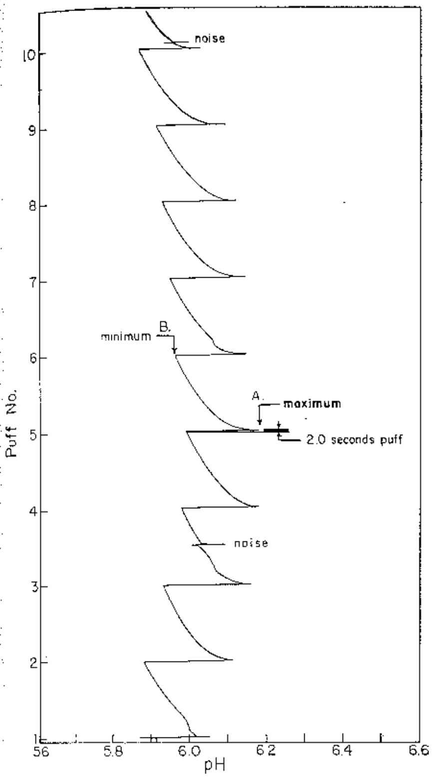

Figure 3. Typical pH recording of smoke.

trode in pH 7 buffer solution.

Experimental

Several filter and nonfilter blended cigarettes were analyzed by the procedure using the system shown in Figure 1B. A typical pH recording for a blended filter cigarette is illustrated in **Figure 3.** The pH increases while the puff is being taken to a maximum then slowly decreases to a minimum just before the succeeding puff is taken. During the smoking process the pH minimum increases for the first few puffs, remains constant for several puffs, then tends to decrease on the last few puffs. The decrease is more pronounced when smoking nonfilter cigarettes as opposed to filter cigarettes. Smoke from most blended cigarettes yields pH values in the 5.80 to the 6.00 range with essentially the same shape curve.

Although the recording provided the most detailed information, it was still desirable to arrive at specific pH values for individual cigarettes. The values usually reported included the mean of the minima and the mean of the maxima for the last eight puffs. In addition the individual high and low maximum values and high and low minimum values were recorded to more clearly define the type of tobacco being smoked.

Table 1 lists representative results realized from smoking several types of cigarettes. Twelve determinations of the pH were made using the 85-mm. cellulose acetate filter cigarette. The mean for the minimum pH was 5.91 and the mean for the maximum pH was 6.14 for these twelve determinations. The standard deviation was 0.035 for the mean minimum pH and 0.033 for the mean maximum pH.

Smoke from blended cigarettes with activated charcoal in the filter yielded pH values somewhat higher than both nonfilter cigarettes and cigarettes with regular cellulose acetate filters. This is illustrated in **Figure 4** which shows pH curves for these types of cigarettes.

Figure 5 shows the pH curves obtained from smoking cigarettes made from three different grades of flue-cured tobacco. The tobacco in Sample A was lowest in nicotine and

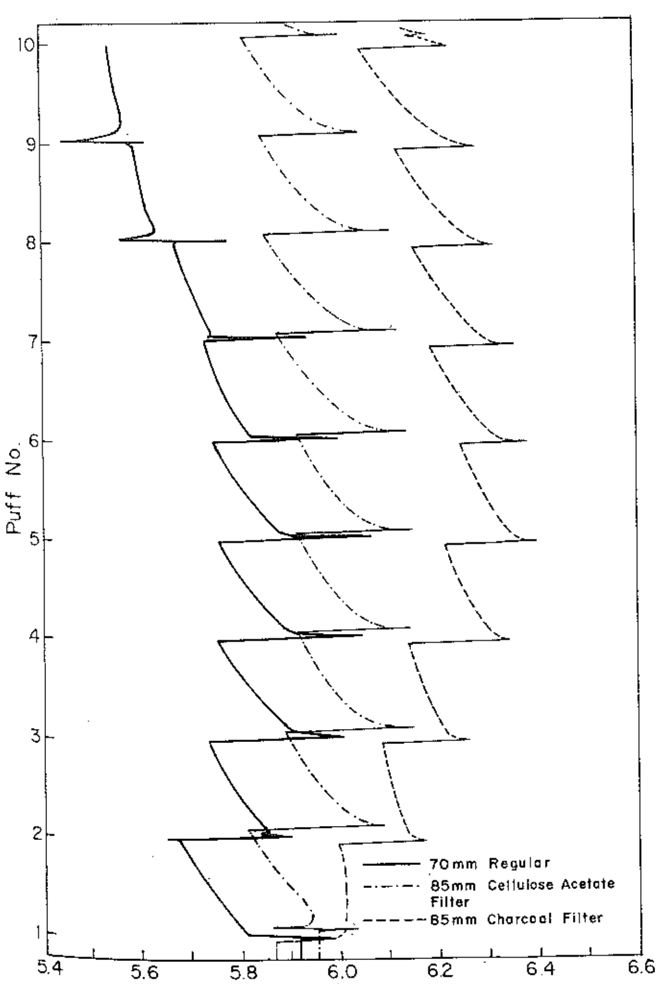

Figure 4. pH Recordings of blended tobacco smoke.

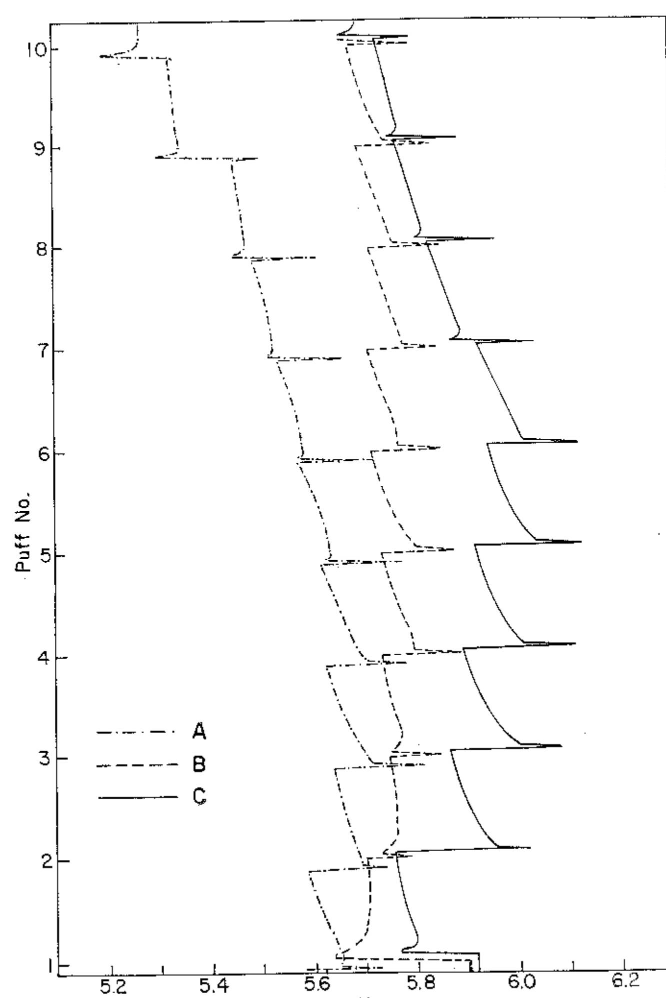

Figure 5. pH Recordings of flue-cured tobacco smoke.

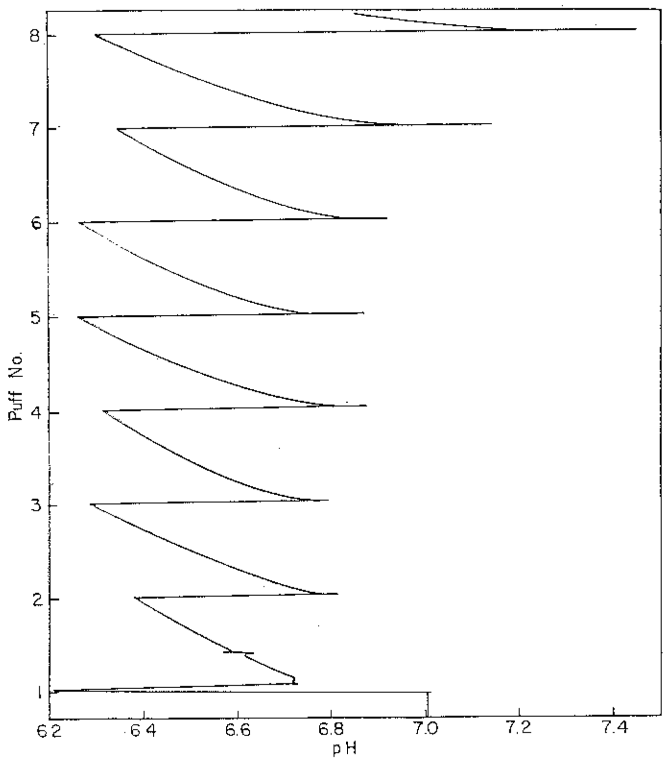

Figure 6. (a). pH Recording of burley tobacco smoke.

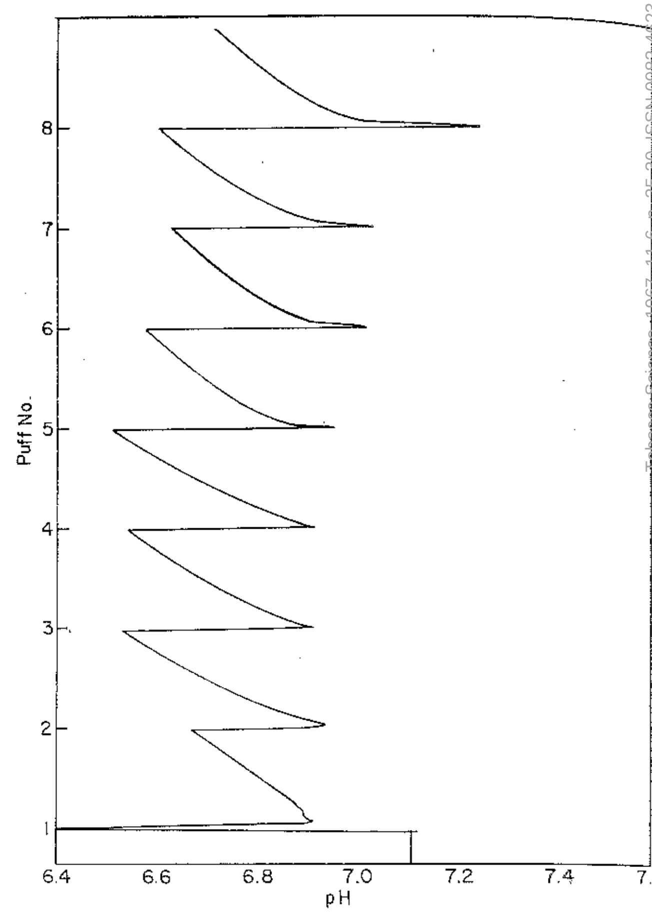

Figure 6. (b). pH Recording of burley tobacco smoke.

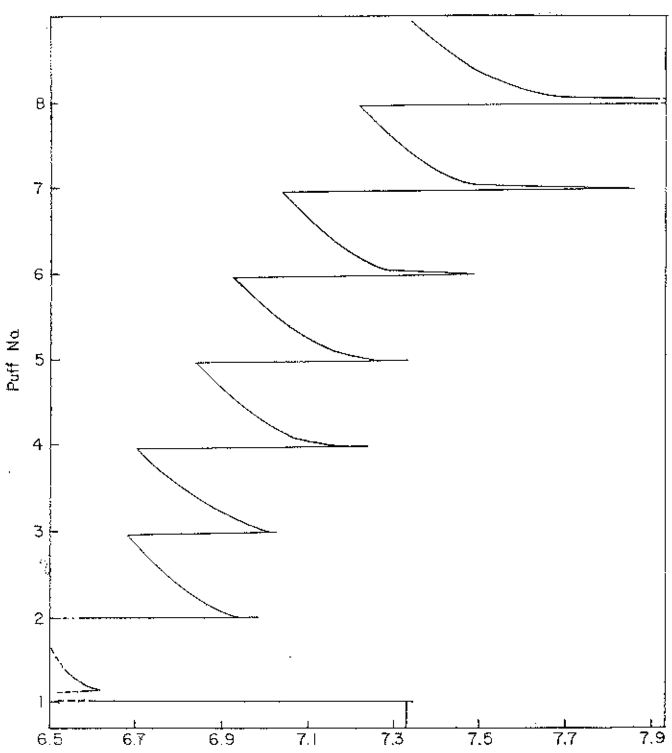

Figure 6. (c). Recording of burley tobacco smoke.

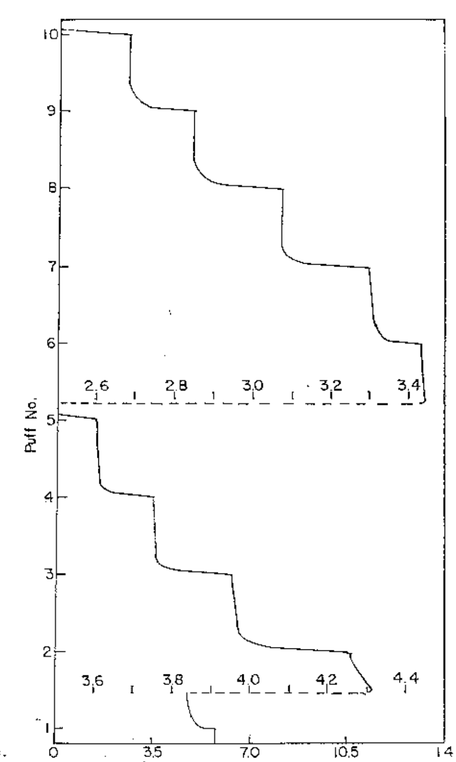

Figure 7. pH Recording of cellulose smoke.

highest in sugar content; in Sample C was highest in nicotine and lowest in sugar content; in Sample B was intermediate in both nicotine and sugar content. The curve for Sample C closely approximates that realized from a regular blended cigarette.

Figures 6a, b, and c show the pH curves realized from smoking cigarettes made from three grades of uncased burley tobacco. The burley tobacco cigarettes used in **Figure 6a** contained a low amount of nicotine, whereas the one used in **Figure 6c**

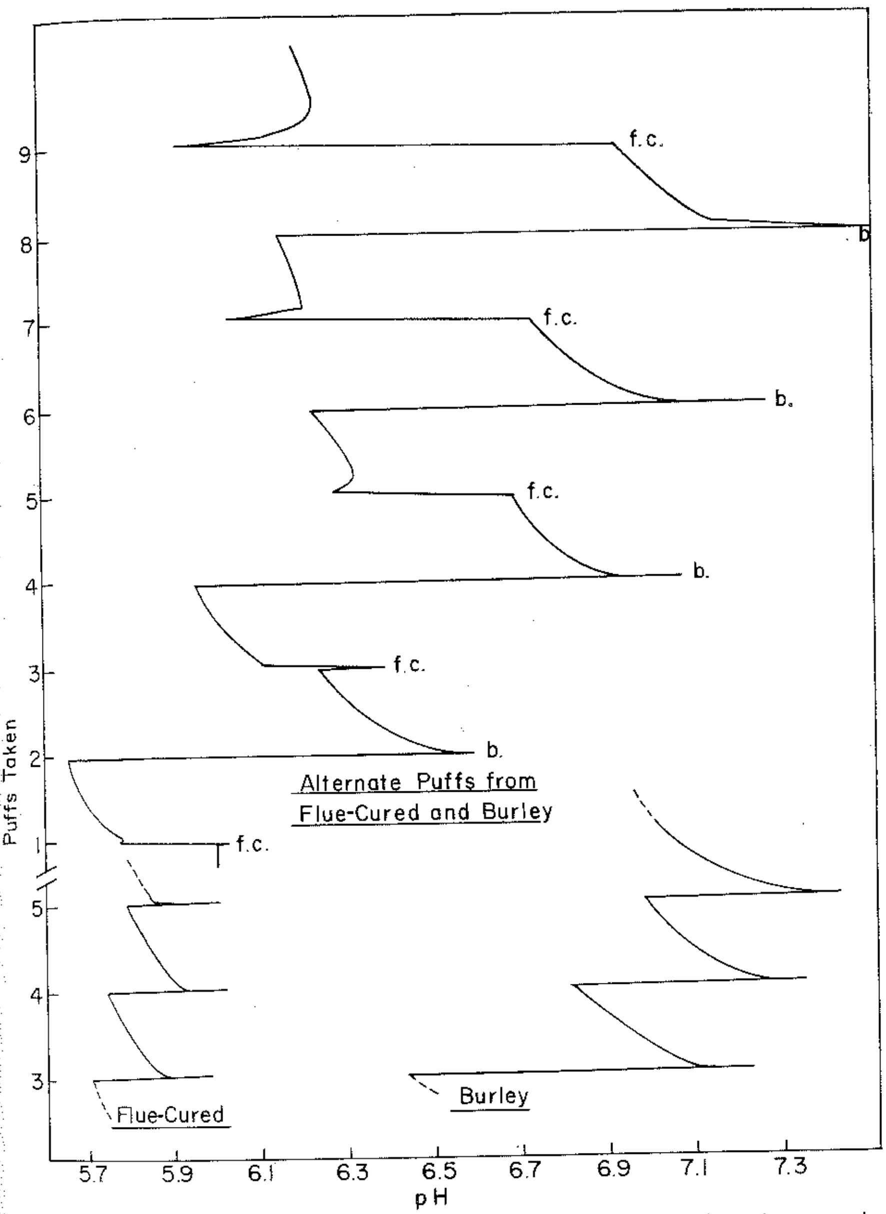

Figure 8. Response of the system to alternate puffs of flue-cured and burley tobacco smoke.

contained a high amount of nicotine. The one used in **Figure 6b** was intermediate between the two. The wider spread between maxima and minima, and the significant increase in pH as the cigarette is consumed not only characterize burley tobacco smoke, but emphasize that more than just nicotine is involved in regulating the pH of the smoke.

Cellulose rods were smoked using this technique to determine the type of curve that would be obtained from smoke containing no organic bases, but appreciable quantities of organic acids. It can be seen in **Figure 7** that not only did the pH range drop for the cellulose smoke, but also an entirely different shape curve was realized. The pH dropped sharply during the puff and remained fairly constant until the succeeding puff, whereas in tobacco smoke the pH increased during the puff and decreased until the succeeding puff.

A system was designed whereby controlled amounts of acidic and basic vapor or mixtures of these vapors could be added directly to either a 35-ml. puff of air or smoke. The addition of nicotine or ammonia to 35 ml. of air immediately increased the pH to the 8 or 9 range. Addition of acetic acid vapor to a 35-ml. puff of air immediately reduced the pH to the 4 to 5 range. A mixture of acetic acid and nicotine yielded a curve somewhat similar to the curve observed for cigarette smoke. Proper adjustment of the ratio of nicotine to acetic acid would give a pH curve in the same range of blended tobacco smoke. The addition of more acidic vapor such as HCl would immediately decrease the pH to a zero reading.

Direct addition of acetic acid or nicotine to the smoke aerosol brought about a change in pH; however, this change was slower and not of the magnitude as the change observed upon addition of these vapors to a 35-ml. puff of air.

The effect of one puff on the pH of the following puff was demonstrated by taking alternate puffs from a flue-cured cigarette and a burley cigarette. As shown in **Figure 8**, a large difference was noted between the pH of the puffs; however, it was not as large as if the two cigarettes were smoked separately. The passage of air across a clean electrode equilibrated at pH 6 had only a minor effect on the film in that a slight decrease of a few hundredths of a pH unit was observed; however, if air was passed across an electrode with smoke deposits on it, a definite change in pH was observed. The passage of air across the electrode would be expected to remove some of the volatile material which would affect the pH of the smoke film. Any condition which brings about a change in the acid-base ratio of the film on the electrode will result in a pH change whether the result is the loss or gain of an acidic or basic component.

Discussion

Examination of the curve profile of a single puff shows that the interaction of the smoke components and the film on the electrode is very dynamic. Assuming the change in potential to be due entirely to a pH change of the aqueous film on the electrode, then it is apparent that the mechanism for transfer of the acidic and basic components to that film depends upon several factors. During the puff the pH rises sharply indicating either the loss of acid from the film or the gain of base in the film. After the puff has been taken, a sharp decrease in pH is observed which indicates either a loss of basic material from the film or the adsorption of acidic material in the film. Since smoke is an aerosol consisting of both vapor and particulate phases, each in all probability having different pH characteristics, it would be expected that they would affect the pH differently under the dynamic conditions during the puff and the less dynamic conditions after the puff has been taken. The most likely explanation of the puff profile curve would be adsorption of the more basic fraction during the puff and then reaction of the film with the more acid vapor phase of the smoke after the puff. However, the complexity of the aerosol, the interaction of the smoke fraction deposited on the electrode and the vapor phase, the rate of solution, the rate of reaction, and the other different dynamic conditions of the smoking cycle would require extensive investigation before an accurate explanation of the curve could be realized. Since the glass electrode is specific to hydrogen ion concentration, the values observed are indicative of the acid-base ratio of smoke and can be used to make comparative tests for cigarette smoke using the described conditions. This was demonstrated with the addition of basic and acidic vapors to smoke. The effects of the acid-base ratio change by those additions were readily observed.

Obtaining the 5.9-6.1 pH range before smoking is not critical for different types of tobacco that yield large amounts of basic material; however, when comparing blended cigarettes, it is important that a constant reference point be established. The electrode can be buffered to any desired pH by use of the proper buffer solution. Unless most of the buffer solution is removed from the electrode, the shape of the curve as well as the reproducibility will be considerably affected. A small piece of chamois skin, dampened with the buffer solution, has been used with good results for leaving a uniform film on the electrode.

The procedure is an empirical one and the results will depend upon the conditions under which the measurements are made. It should find its main utility in comparative work. The techniques employed in this study could probably also be applied to different types of electrode systems such as the electrodes investigated by Kamienski (4) and yield more information on the oxidizing and reducing characteristics of smoke.

Literature Cited

1. Grob, K. Determination of the pH Value and Buffering Capacity of Cigarette Smoke as a Routine Method. *Beitr Tabakforsch.* 3:97-100. 1961.
2. Kamienski, M. B. Potentiometric Chromatography. Part II. A Microelement for the Detection of Weak Acids and Bases in Gasoline Solutions. *Polska. Akademia Umiejet. Krakow. Wykziat. Matemat. Przyrod. Bull. Intern. Ser. A. Sciences Math.* 1950:75-80. 1950.
3. Kamienski, M. B. An Electric Microelement as a Detector of Small Concentrations of Acid, Basic, Oxidizing, and Reducing Substances in non-Conducting Liquids and Gases. *Polska. Akademia Umiejet. Krakow. Wydziat. Matemat. Przyrod. Bull. Intern. Ser. A. Sciences Math.* 1950:81-86. 1950.
4. Kamienski, M. B. Application of the Adsorption Microelement to the Detection of Acid, Basic, Oxidizing and Reducing Impurities in Gases. *Polska. Akademia Umiejet. Krakow. Wydziat. Matemat. Przyrod. Bull. Intern. Ser. A. Sciences Math.* 1950:87-89. 1950.
5. Kamienski, M. B. Preparation and Testing of the Electrometric Adsorption Element. (Potentiometric Chromatography). Part III. *Polska. Akademia Umiejet. Krakow. Wydziat. Matemat. Przyrod. Bull. Intern. Ser. A. Sciences Math.* 1950:157-60. 1950.
6. Kamienski, M. B. Electrometric Selective Adsorption. The Antimony Electrode. Potentiometric Chromatography. Part IV. *Polska. Akademia Umiejet. Krakow. Wydziat. Matemat. Przyrod. Bull. Intern. Ser. A. Sciences Math.* 1950:171-182. 1950.
7. Kamienski, M. B., I. Kulawik and I. Mazur. Alumina Gel as an Adsorption Layer in Potentiometric Chromatography. *Bull. Acad. Polon. Sci. Ser. Sci., Chim., Geol. and Geograph.* 6:97-99. 1958.
8. Kamienski, M. B., I. Kulawik and I. Mazur. Influence of the Thickness of Alumina Gel Adsorption Layers on the Potential of Antimony Microelectrodes. *Bull. Acad. Polon. Sci. Ser. Sci., Chim., Geol. and Geograph.* 6: 101-104. 1958.
9. Kobashi, Y., S. Sakaguchi, and M. Izawa. Combustion Temperatures of Some Unblended Cigarettes and the Transfer of Nicotine into Cigarette Smoke. *Bull. Agr. Chem. Soc., Japan* 24:274-277. 1960.
10. Kukonka, A., and B. Rackow. The Acidifying and Colloidal Behavior of Emulsified Tobacco Smoke of Different Origin. *Deut. Gesundheitsw.* 14:1944-1951. 1959.
11. Laurene, A. H., L. A. Lyerly, and G. W. Young. Direct Vapor Chromatographic Determination of Acetaldehyde, Acrolein, and Acetone in Cigarette Smoke. *Tobacco Sci.* 6:25-27. 1962.
12. Pyriki, C., and W. F. Homann. Chinese Tobaccos II. Further Characteristics of These Tobaccos and the Correlations Between Their Chemical Composition and Commercial Quality. *Ber. Inst. Tabakforsch. Dresden* 6:106-118. 1959.
13. Shmuk, A., and M. Kolesnik. The Reaction of Tobacco Smoke in Connection with the Quality of Tobacco. *Narkomsnao SSSR-Soyuztabak Gosudarstvennyi Institut Tabak wedeniya Bull.* 80: 45-52. 1931.