A Simple Technique for Determining the pH of Whole Cigarette Smoke*

by

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SUMMARY

A new technique has been developed to determine the pH of whole cigarette smoke. In this technique, whole smoke from ten cigarettes was trapped in 300 mL water containing 1% (*w/v*) sodium chloride and the pH was determined on the resulting aqueous suspension of cigarette smoke. Two impingers with an extra coarse porosity fritted disc were used to dispense the smoke in the aqueous trapping medium. Cigarettes were smoked on a 20-port Borgwaldt RM 20/CS smoking machine using modified FTC (Federal Trade Commission) conditions. The puff volume was adjusted to take a 35 mL puff as measured through the cigarette and the collection traps. This new technique accounts for the contributions to smoke pH from both the vapor phase and the particulate phase of smoke. The repeatability of this new technique was determined on eighteen replicates of a commercially available non-menthol, filter cigarette. Each measurement was done on a different day to check for a possible drift in pH with time. The mean pH value for the chosen sample was found to be 4.97 with a standard deviation of 0.07 pH units. The smoke pH values for over 150 commercially available cigarette brands with a variety of "tar" levels were determined. The smoke pH values had a range from 4.6 to 5.5, with an average of 4.79 and a maximum standard deviation of 0.10 pH units. An experimental flue cured cigarette had a smoke pH of around 5.0, while an experimental Burley cigarette had a smoke pH of 5.4. No correlation between smoke pH and "tar" or total particulate matter (TPM) and between pH and nicotine levels was found.

The purpose of the present study was to develop a practical, relatively simple laboratory method to measure the pH of a water solution of whole smoke, and was not intended to reflect, or have direct relevance for any biochemical or biological phenomena such as inhalability of smoke, flavor perception, nicotine absorption, etc." [Beitr. Tabakforsch. Int. 19 (2000) 33–48]

ZUSAMMENFASSUNG

Es wurde eine neue Methode zur Bestimmung des pH-Wertes des Gesamtrauchs von Zigaretten entwickelt. Bei diesem Verfahren wurde der Gesamtrauch von zehn Zigaretten durch 300 mL einer 1%igen wässrigen Natriumchloridlösung geleitet und der pH-Wert der resultierenden wässrigen Suspension von Zigarettenrauch bestimmt. Der Rauch wurde durch zwei Gaswaschflaschen mit einer großporigen Fritte in dem wässrigen Auffangmedium verteilt. Die Zigaretten wurden mit einer 20-Port Borgwaldt RM 20/CS-Rauchmaschine unter modifizierten FTC-Bedingungen (FTC = Federal Trade Commission) abgeraucht. Das Zugvolumen wurde so eingestellt, dass ein 35-mL-Zug durch die Zigarette und die Auffangvorrichtung zustande kam. Durch dieses neue Verfahren wurde der pH-Wert des Gesamtrauchs ermittelt, der sich aus dem Anteil der Gasphase und der Partikelphase ergibt. Die Reproduzierbarkeit dieser neuen Methode wurde durch 18 Wiederholungsmessungen einer im Handel erhältlichen Filtercigarette ohne Menthol ermittelt. Jede Messung erfolgte an einem anderen Tag, um eine

mögliche zeitabhängige pH-Abweichung festzustellen. Der mittlere pH-Wert der untersuchten Cigaretten betrug 4,97 mit einer Standardabweichung von 0,07 pH-Einheiten. Es wurden die Rauch-pH-Werte von mehr als 150 im Handel erhältlichen Cigarettenmarken mit unterschiedlichem Kondensatgehalt bestimmt. Die ermittelten Werte lagen bei 4,6 bis 5,5 pH-Einheiten mit einem Durchschnittswert von 4,79 und einer maximalen Standardabweichung von 0,10 pH-Einheiten. Der pH-Wert einer experimentellen flue-cured Cigarette lag bei 5,0, und der pH-Wert einer experimentellen Burley-Cigarette betrug 5,4. Im Hauptstromrauch korrelierte der pH-Wert weder mit dem Kondensatgehalt oder der Gesamtpartikelmasse noch mit dem Nikotingehalt.

Ziel der vorliegenden Studie war es, eine praktische und relativ einfach durchzuführende Labormethode zur Bestimmung des pH-Werts einer wässrigen Lösung des Gesamtrauchs zu entwickeln. Es war nicht der Zweck dieser Studie, biochemische bzw. biologische Phänomene wie die Inhalierbarkeit von Rauch, die Wahrnehmung von Geschmacksstoffen, die Absorption von Nikotin, etc. zu simulieren oder zu erklären. [Beitr. Tabakforsch. Int. 19 (2000) 33–48]

RESUME

Une nouvelle technique a été mise au point pour calculer le pH de la fumée totale de cigarette. Cette technique consiste à piéger la fumée totale de dix cigarettes dans 300 mL d'eau contenant 1% (*w/v* poids/volume) de chlorure de sodium. Le pH est calculé sur la suspension aqueuse résultante de la fumée de cigarette. Deux impacteurs dotés d'un disque fritté de grande porosité, ont servi à insuffler la fumée dans le milieu de piégeage. Les cigarettes ont été fumées sur une machine à fumer Borgwaldt RM 20/CS à 20 canaux en utilisant les conditions de la FTC modifiées. Le volume de bouffée a été ajusté de façon à obtenir une bouffée de 35 mL, mesurée au niveau de la cigarette et des pièges. Cette nouvelle technique rend compte des contributions au pH de la fumée à la fois de la phase gazeuse et de la phase particulaire. La reproductibilité de cette nouvelle technique a été calculée sur dix-huit répliques d'une cigarette filtre non mentholée vendue dans le commerce. Chaque mesure a été effectuée à des jours différents pour vérifier toute variation possible du pH en fonction du temps. Le pH moyen de l'échantillon choisi était de 4,97, avec un écart type de 0,07. Le pH de la fumée de plus de 150 marques de cigarettes vendues dans le commerce possédant différents teneurs en goudrons ont été évalués. Ces valeurs variaient de 4,6 à 5,5, avec une moyenne de 4,79 et un écart type maximum de 0,10. Dans le cas d'une cigarette expérimentale de type virginie (flue-cured), le pH était d'environ 5,0, tandis qu'une cigarette expérimentale de type Burley

présentait un pH d'environ 5,4. Aucune corrélation n'a été établie entre le pH de la fumée et les teneurs en goudrons ou de la matière particulaire totale (MPT) et de nicotine.

L'objectif de cette étude a été d'élaborer une méthode de laboratoire pratique et relativement simple permettant de mesurer le pH d'une solution d'eau de fumée totale, et non pas de refléter ou d'établir un rapport direct à un quelconque phénomène biochimique ou biologique, tel que l'inhalation de la fumée, la perception du goût et l'absorption de la nicotine. [Beitr. Tabakforsch. Int. 19 (2000) 33–48]

INTRODUCTION

The determination of smoke pH commonly requires a dispersion of smoke in water or at least in a partially aqueous medium that contains water and an organic solvent. Mainstream cigarette smoke (MSS) is a highly concentrated aerosol (1) that consists of over 500 vapor-phase components (2) and over 4000 particulate-phase components (3). Carbon dioxide, carbon monoxide (both in the vapor phase), water, nicotine, triacetin, propylene glycol, glycerol, and acetic acid (all mainly in the particulate phase) account for over ninety weight-percent of the MSS of a typical American filter cigarette (4). These compounds with the exceptions of carbon monoxide and triacetin are quite soluble in water; however, many other components of smoke are sparingly, if not totally insoluble in water. Thus, any effort to measure the pH of MSS will involve deviation from the classical definition of pH for true aqueous solutions (5,6,7).

The use of nonclassical pH measurements has been reported for other matrices. Some examples include processed foods (8), fruits and vegetables (9), flour (10), bread dough (11), peat (12), water-insoluble phenol-formaldehyde resins (13), rain and fog (14), and unsmoked tobacco (15). All these are empirical approaches, and there are no references in the literature that satisfactorily describe the theoretical basis for the pH of suspensions or semi-solids. Also, it is still impossible to base the pH measurement in partially aqueous solvent mixtures on the standard pH scale in water (5).

Therefore, tobacco chemists have taken various empirical approaches for the determination of smoke pH. All the techniques were developed to meet the needs in the laboratories at the time the work was done (16, 17, 18). The smoke pH values thus obtained depend upon the method used and on whether total smoke or only the particulate phase is collected. The topic of smoke pH was recently reviewed as part of a general review of analytical chemistry for tobacco and tobacco smoke (16).

There have been several approaches for the determination of smoke pH:

A ▶ The determination of the pH of an aqueous suspension of the total particulate matter as originally developed by GROB (19, 20, 21).

B ▶ The determination of the pH of the smoke aerosol that is absorbed by an aqueous film around a pH electrode as originally developed by SENSABAUGH and CUNDIFF (22).

C ▶ The determination of an aqueous suspension of smoke condensate collected in cold traps (23).

D ▶ The determination of smoke pH by collecting whole smoke in water using a high shear agitator and further removing the carbon dioxide and other vapor phase components using forty clearing puffs, as developed by HARRIS and HAYES (24).

E ▶ The determination of whole smoke pH as originally done by SHMUK (17) and as further developed by BRAUMANN and ELMENHORST in 1989 (18).

Of these approaches, the one developed by GROB with his later modification to use a Cambridge pad instead of a cotton filter to collect the TPM (21) has been very popular because of its ease of use. Cigarettes are smoked by one of the routine methods commonly employed, and the TPM is collected in the same manner as for the routine determination of "tar" and nicotine. The pad is then slurried in water that is free of carbon dioxide. The pH is determined on the resulting aqueous slurry after removing the pad.

There are two assumptions implicit in the use of GROB's approach. First, the contributions to smoke pH from the components of the vapor phase must be neglected. Second, the Cambridge pad does not in itself contribute to the resulting determination of smoke pH. This latter point appears to be sometimes ignored, although the influence of the pad was noted by GROB in 1966 (21). Furthermore, similar filters have been used for the collection of atmospheric particulate matter and artifact formation caused by the alkalinity inherent in glass fiber filters is well known (25). Indeed, pH values as high as 9.9 have been reported for aqueous extracts of such filter media (26).

Pad alkalinity as high as 169 $\mu\text{eq/g}$ of filter material has been measured for glass-fiber filters of similar construction to Cambridge filter pads (27). Given that a 44 mm Cambridge filter weighs about 0.3 g, one could expect between 20 and 50 μeq of alkalinity for each pad. Acetic acid is the main particulate phase acidic decomposition product of sugars and concentrations between 70 to 120 $\mu\text{g/cigarette}$ (1.2 to 2 μeq) were reported for filter cigarettes (28, 29, 30). Since five cigarettes per pad are typically used for smoke pH measurements, this gives 6 to 12 μeq of acidity as acetic acid. Therefore, pad alkalinity can easily overcome any natural smoke acidity, thus causing the determination of an artificially high pH value. This is a severe disadvantage of the GROB method, particularly when smoke pH is taken out of context (31, 32).

The use of TPM alone for the determination of smoke

pH is not adequate to describe the whole effect of smoke regarding its hydrogen ion activity. Methods that look at whole smoke should be utilized. Indeed, something as simple as measuring the pH with pH paper in the smoke stream has been tried (33). However, the results were published only for plain-end cigarettes made in East Germany during the first few years after World War II, or for fermented tobaccos (34). This technique is not accurate enough and did not give a finite pH value, but only a range for the smoke pH.

Another technique for the determination of smoke pH is that developed by SENSABAUGH and CUNDIFF (22). In their paper, they stated that the technique developed by GROB (19) did not account for the contributions of vapor-phase acids and bases to smoke pH. The authors redefined the concept of smoke pH to mean the pH of a thin aqueous film on the surface of a modified combination pH electrode after being exposed to the mainstream smoke (22). Also, they stated that their procedure was an empirical one; and that for blended cigarettes, it was important to adjust the pH meter to give a value between 5.9 and 6.1 before lighting the cigarette (22). While the SENSABAUGH and CUNDIFF technique was cited early on as a preferred technique for the determination of smoke pH (35), it also has been held in disrepute because it is difficult to use, it may give erratic results (36) and does not truly account for the contribution of vapor phase to smoke pH (24). A modification of the electrode used in the SENSABAUGH and CUNDIFF's technique has also been reported (37).

A common technique for the determination of smoke pH is the one developed by HARRIS and HAYES (24). HARRIS and HAYES stated that they were looking for a technique that was more efficient and easier to use than that of SENSABAUGH and CUNDIFF. They used an in-house designed twenty-port rotary smoking machine to generate the smoke. The smoke was then passed into 50 mL water in a high-shear agitator. After the cigarettes were smoked, forty clearing puffs were taken to remove the excess carbon dioxide. The pH was then determined on the degassed mixture after dilution with 50 mL water. In spite of the title "...whole smoke", this method does not account for the carbon dioxide contribution to smoke pH. The volume of water used to collect the smoke from twenty cigarettes was only 50 mL. In this volume of water, less than 10% of MSS carbon dioxide can be absorbed (excluding chemical reactions). In addition, the clearing puffs taken at room temperature as indicated in the original paper, will eliminate most of the solubilized carbon dioxide. The authors stated that they needed to use the clearing puffs to get similar values as they obtained with the technique developed by SENSABAUGH and CUNDIFF (22). This step artificially raises the measured pH. Since smoke pH has been alleged to control the amount of unprotonated

Figure 1.
Setup for smoke trapping.

nicotine in the smoke (31), then any measurement conditions that artificially changed the pH must be avoided.

Smoke pH also has been determined on whole smoke condensate that has been trapped in cold traps and then slurried in water after being removed from the traps (23). However, no details were given on the precautions taken, if any, to conserve the gases that may have been trapped in the condensate.

One other technique for determining smoke pH is the trapping of smoke in water and then determining the pH on the resulting aqueous slurry. The most attractive feature about this technique is that it measures the entire smoke and does not involve any artificial barriers such as the Cambridge pad. As noted earlier, this approach was first recommended by SHMUK (17) in 1931. It was also used by BETTS and by ELSON and co-workers (30, 38).

The present work was done with the goal of overcoming some of the objections to the use of whole smoke in pH determinations. In this technique, whole smoke is collected in water by passing it through two impingers. The amount of water has been chosen such that the possibilities of supersaturation of the water with carbon dioxide have been minimized. Also, the smoking machine has been adjusted to account for the pressure drop across the two impingers. Furthermore, measurements were conducted on the vapor phase of smoke (including carbon dioxide) and the total particulate phase (including acetic and formic acids) for the evaluation of the trapping efficiency.

The purpose of the present study was to develop a practical, relatively simple laboratory method to measure the pH of a water solution of whole smoke, and was not intended to reflect, or have direct relevance for any biochemical/biological phenomena such as inhalability of smoke, flavor perception, nicotine absorption, etc.

EXPERIMENTAL

Smoke collection

Figure 1 shows the trap set-up for smoke collection. It consists of two impingers in series followed by a Cambridge filter. Each impinger (Fisher Scientific), has a capacity of 250 mL, an approximate height of 300 mm, a fritted disc with a diameter of 20 mm and 8 mm o.d. connecting tubes. The fritted disc has an extra coarse porosity, which provides uniform dispersion of smoke bubbles in the water.

Fresh deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$, purified with a Millipore Milli-Q system) with 1% (*w/v*) sodium chloride was used. Water was initially degassed by bubbling nitrogen through it for about twenty minutes. The sodium chloride was added to increase the conductivity of pure deionized water and facilitate the pH measurement. Each trap contained 150 mL water.

The impingers were cleaned after each determination by washing them with hot isopropyl alcohol for ten minutes and then drying in an oven at 150°C for twenty minutes.

Smoking machine adjustment

A Borgwaldt RM 20/CS smoking machine was used in this study. Since the water traps create a pressure drop of about 40 cm water, an important objective in this study was to optimize the conditions for the collection of the smoke so that more accurate pH measurements could be done. In order to ensure a standard puff volume through the cigarette and the water traps, the smoking machine settings had to be adjusted. The smoking machine was set to a 2.4 sec. puff duration and 40 mL puff volume to obtain a 35 mL puff volume through the cigarette and collection system. After this adjustment, the smoke profiles were measured. Figure

2 curve (a) illustrates the profile of a cigarette smoked similar to FTC standard conditions (35 mL per puff of 2 sec. duration, 1 min. intervals). Figure 2 curves (b) and (c) illustrate the profiles measured using two water traps before and after the adjustments, respectively. The comparison indicated that without the adjustments only about 25 mL of each puff, as seen in Figure 2 curve (b), passed through the traps while 35 mL was obtained after the adjustments.

For each determination, ten cigarettes were smoked after they had been conditioned for at least 24 hours at 60% RH and 22 °C. The cigarettes were neither weight nor pressure-drop selected. At the end of the smoke run, three clearing puffs were taken.

pH Meter calibration

A Fisher Scientific Accumet 15 pH meter with a microprocessor and a solid state pH probe was used for the pH measurements. The pH meter was calibrated with standard buffer solutions at pH 4 and pH 10. The electrode was washed completely with deionized water before and after each measurement. The cleaned electrode was stored in deionized water between pH determinations. After collection of the smoke, the aqueous contents of the traps were combined and were gently stirred with a magnetic stir bar, followed by immersion of the electrode for the pH measurement. All the data were recorded at 3.0 minutes after the immersion of the electrode.

GC/MS conditions for the analysis of vapor-phase components

Vapor-phase components from smoke collected without the water traps and after exiting the water traps were analyzed by a GC/MS procedure. The vapor phase was collected in a 7 L gas bag, and the sample was transferred to a 1 mL gas loop for GC/MS analysis. The separation for vapor phase components was done on a DB1 column (60 m × 0.32 mm i.d. × 1 μm

film thickness) with a temperature program from -50 °C to 140 °C. Peaks were identified by MS library search.

GC/MS conditions for the analysis of total particulate matter

The total particulate matter from the smoke of ten cigarettes was collected in a system using the water traps, with a regular Cambridge pad between the traps and the smoking machine. An identical sample was collected without the water traps. The pads were extracted with 20 mL *n*-butyl methyl ether (TBME) for GC/MS analysis. The extract from the TPM collected without water traps was injected directly into the GC/MS system. However, because the water traps retained much of the particulate phase, the corresponding pads had only a very small quantity of TPM. This TPM was initially dissolved in 20 mL of TBME, but the volume was reduced to 0.5 mL (forty times concentrated) for the GC/MS analysis. The concentration was done by evaporating TBME under a stream of nitrogen. Modifications in the composition of this extract during the evaporation are not expected because only compounds with low or moderate volatilities are present on the pad. The GC/MS separation was done on a DB5 column (60 m × 0.32 mm i.d. × 1 μm film thickness), with an oven temperature program from 35 °C to 300 °C. Peaks were identified by MS library search.

RESULTS AND DISCUSSION

In this approach, water was chosen to collect whole smoke in order to avoid any complications related to the definition of pH in partially aqueous solvent mixtures. However, whole smoke is not completely soluble in water. A study was done to establish the optimum amount of water in the traps in order to minimize TPM or vapor-phase losses. There are many smoke components that could make contributions to smoke pH. Those compounds include alkaloids (such as nicotine), carbon dioxide, phenols, organic acids (such as formic and acetic acids), and traces of pyridines, pyrazines, ammonia, etc. The amount of these components may be important when considering their contribution to smoke pH.

Carbon dioxide has its own influence on smoke pH by the formation of carbonic acid. For example, a Kentucky 1R4F reference cigarette delivers 42 mg carbon dioxide per cigarette in its mainstream smoke (3). Smoking ten cigarettes would generate about 0.0095 moles carbon dioxide, corresponding to a volume of about 212 mL under standard conditions. The solubility of carbon dioxide in water (39) is 759 mL/L at

Figure 2.
Puff profiles: a) FTC standard; b) two impingers, not corrected; c) corrected with two impingers.

Table 1.
Carbon dioxide trapping efficiencies.

Cigarette	Regular smoking (mg/cig.)	With water traps (mg/cig.)	Trapping efficiencies (%)*
Full Flavor KS **	53.30	33.25	38
Lights KS	45.14	33.41	26
Ultra Lights KS	19.00	7.41	61

*Trapping efficiency was calculated as the ratio $(CO_{2\text{ FTC}} - CO_{2\text{ with water traps}}) / CO_{2\text{ FTC}}$ expressed in percentage.

** KS = King Size

25 °C and 760 mm pressure. Thus, a minimal volume of 280 mL of water must be used. In this work, the total water volume in the traps was chosen to be 300 mL. A larger volume would introduce too much dilution, particularly for ultra low TPM cigarettes. Also, an additional problem with a larger volume of water is that it would increase the pressure drop across the trapping system. This would cause too much modification of the puff profile.

The trapping efficiency for carbon dioxide was evaluated by analyzing the carbon dioxide level in the vapor phase exiting the two traps. For this purpose, ten cigarettes were smoked through the traps and the amounts of carbon dioxide produced with and without the traps were compared. The results for several cigarette brands are given in Table 1.

WINGATE and co-workers recently reported data from a similar study (40). They reported the trapping efficiencies for carbon dioxide for the mainstream smokes of several Kentucky reference cigarettes. Their results are shown in Table 2.

Table 2.
Carbon dioxide trapping efficiencies as reported by WINGATE and co-workers (40).

Cigarette	Trapping efficiencies (%)
2R1F (Full Flavor KS)	38
1R3F (Full Flavor KS)	48
1R5F (Ultra Lights KS)	45

The data in Table 2, although generated by a different technique, show that our data are comparable and that there is not a consistent relationship between TPM deliveries and trapping efficiencies for carbon dioxide. Our data indicated that the use of two water traps was not effective enough to absorb all the carbon dioxide. However, based on the amount of carbon dioxide generated from 1R4F cigarettes and on 300 mL water, a calculation for carbon dioxide alone shows a pH of 3.93 for 100% absorption, a pH of 4.08 for 50% ab-

sorption, and a pH of 4.14 for 38% absorption of the total amount of carbon dioxide. The smoke pH for vapor phase was collected for three cigarette brands, including a 1R4F Kentucky reference cigarette. The results are shown in Table 3. As seen from this table, the pH of vapor phase alone is around 4.3. This value is slightly higher than the calculated value for carbon dioxide alone, indicating that other vapor phase components may have some contribution to smoke pH.

Besides carbon dioxide, the absorption of other vapor-phase components in water was also incomplete. Figure 3 shows the total ion chromatograms (TIC) generated by GC/MS analysis of vapor phase from 1R4F cigarettes smoked under regular FTC smoking conditions (Figure 3a) and with trapping in water (Figure 3b). The identified compounds are listed in Table 4, together with their corresponding normalized area count values obtained using flame ionization detection. Figure 3 and Table 4, indicate that polar compounds were trapped in the water. Such compounds included acetaldehyde, acrolein, acetonitrile, acetone, 2-methylpropanal, propanenitrile, 3-buten-2-one, butanone, 2-methylbutanal. Only partial absorption of hydrocarbons and of other non-polar compounds took place in water.

The trapping efficiency for TPM was evaluated by collecting the TPM exiting the water traps as shown in Figure 1. The weight difference of a Cambridge filter pad placed behind the water traps was measured before and after smoking ten cigarettes. Percent loss of TPM was calculated based on the measured TPM and the nominal FTC TPM value for a given cigarette. A low TPM loss indicated good trapping efficiency (measur-

Table 3.
Smoke pH for vapor phase trapped in water.

Cigarette	Average pH of vapor phase only	Standard deviation
1R4F	4.30	0.09
Full Flavor KS	4.28	0.04
Ultra Lights KS	4.44	0.03

Figure 3.
Total ion chromatograms of vapor phase for 1R4F cigarettes: a) regular smoking; b) smoked with two water traps.

ing the trapping efficiency % as $100\% - \text{loss \%}$. Table 5 shows the TPM losses for a series of experiments with a common commercial cigarette. As seen in this table, the TPM loss varied from run-to-run with a maximum of 1.36%.

Table 6 shows the TPM losses for several other cigarette brands. For Full Flavor cigarettes, the TPM loss was in the range of 0.3% to 0.8%. However, for other styles and mainly for Ultra Lights cigarettes, the TPM loss percentage was higher although the absolute loss was rather low. The data from this study compare favorably with those reported by WINGATE and co-workers (40). The composition of TPM obtained with the use of water traps was analyzed and was found to be different from the TPM obtained without the water trap. The water content of the TPM obtained with the use of water traps was not different from common values for the water in TPM (about 8%). However, significant

differences can be seen when comparing the TICs shown in Figure 4. These TICs were generated by a GC/MS analysis of the TPM collected on a Cambridge pad from regular smoke, and from smoke after water traps as used in smoke collection for pH measurement, respectively. Because the TPM level on the Cambridge filter after the water traps was very low, the sample was concentrated forty times before analysis (as indicated in the experimental part).

The difference between the chromatograms shown in Figure 4 indicates that the trapping efficiency for different components varied, probably depending on their solubilities and polarities. Some identifications for the peaks numbered in the chromatograms are given in Table 7. As seen in Table 7, a significant number of compounds in the TPM collected after the water traps were long chain hydrocarbons. Quantitations were done only for selected compounds. As an example,

Table 4.

Comparative flame ionization detection area counts (normalized) of selected vapor-phase components for a 1R4F cigarette between regular smoking and smoked with two water traps.

Peak no.	Compound	Chemical Abstract no.	Regular smoking	With water traps	Reduction (%)
1	hydrogen sulfide	7783-06-04	0.05	0.04	20
2	propene	115-07-1	18.0	12.1	33
3	propane	74-98-6	13.9	10.0	28
4	methylene chloride	74-87-3	3.4	2.0	41
5	2-methylpropane	75-28-5	1.2	1.0	17
6	acetaldehyde	75-07-0	21.2	n.d.	100
7	1-butene	106-98-9	5.4	3.0	44
8	butane	106-97-8	3.7	2.8	24
9	butadiene	590-19-2	4.2	2.8	33
10	methanol	67-56-1	1.1	n.d.	100
11	2-butene	624-64-6	2.4	1.7	29
12	methanethiol	74-93-1	1.0	0.4	60
13	2-methyl-1-propene	115-11-7	2.1	1.4	33
14	2-methyl-1-butene	563-46-2	1.1	0.8	27
15	2-methylbutane	78-78-4	1.0	0.7	30
16	1-pentene	109-67-1	0.8	0.8	0
17	acrolein	107-02-8	3.0	n.d.	100
18	acetonitrile	75-05-8	4.1	n.d.	100
19	acetone	67-64-1	11.7	n.d.	100
20	furan	110-00-9	3.1	2.2	29
21	propanal	123-38-6	2.1	n.d.	100
22	isoprene	78-79-5	31.1	23.9	23
23	2-pentene	109-68-2	3.9	3.1	21
24	1,3-pentadiene	1574-41-0	0.8	0.6	25
25	1,3-cyclopentadiene	542-92-7	2.1	1.5	29
26	2-methylpropanal	78-84-2	1.0	n.d.	100
27	propanenitrile	107-12-0	1.0	n.d.	100
28	3-buten-2-one	78-94-4	1.4	n.d.	100
29	1-hexene	592-41-6	1.1	0.8	27
30	2,3-butanedione	431-03-8	1.2	n.d.	100
31	butanone	78-93-3	3.2	n.d.	100
32	2-methylfuran	534-22-5	1.8	1.1	39
33	2-methyl-2-pentene	625-27-4	1.0	0.7	30
34	benzene	71-43-2	3.9	1.9	51
35	2-methylbutanal	96-17-3	0.5	n.d.	100
36	heptane	142-82-5	0.6	0.4	33
37	2,5-dimethylfuran	625-86-5	0.8	0.5	38
38	toluene	108-88-3	2.8	1.9	32
39	ethylbenzene	100-41-4	0.1	0.1	0
40	1,2-dimethylbenzene	95-47-6	0.1	0.1	0
Average reduction (%)					50

Table 5.
TPM losses for a common commercial Full Flavor filter cigarette.

Run	FTC TPM (mg/cig.)	TPM after traps (mg/10 cig.)*	TPM reduction (%)	TPM loss (%)**
1	18.1	0.94	99.48	0.52
2	–	2.50	98.64	1.36
3	–	1.07	99.41	0.59
4	–	1.74	99.04	0.96
5	–	0.49	99.73	0.27
Average		1.63	99.26	0.74

* TPM loss is measured from the weight differences of the Cambridge filter pad placed behind the traps before and after 10 cigarettes were smoked.

** TPM loss (%) was calculated from the TPM of 10 cigarettes (in mg) collected after the water traps divided by the nominal FTC TPM. No correction was made for the pad moisture content.

Table 6.
TPM losses for several commercial cigarettes.

Brands	FTC TPM (mg/cig.)	TPM after traps (mg/10 cig.)*	TPM reduction (%)	TPM loss (%)**
Full Flavor KS A	18.3	1.50	99.18	0.82
Full Flavor KS B	19.2	1.22	99.37	0.63
		0.53	99.72	0.28
Full Flavor KS C	19.2	1.18	99.39	0.61
Medium KS A	13.2	2.65	97.99	2.01
Medium 100's B	14.4	3.73	97.41	2.59
		1.20	99.17	0.83
Medium KS C	11.1	0.91	99.18	0.82
		0.91	99.18	0.82
Ultra Lights KS A	1.3	1.83	–	–
		1.02	92.16	7.84
Ultra Lights KS B (Menthol)	2.5	0.91	96.36	3.64
Ultra Lights KS C (Menthol)	1.3	1.20	91.77	9.23
		1.20	91.77	9.23
Ultra Lights KS D	1.3	2.60	–	–
100% Burley		0.74		
		0.28		
100% Flue-cured		0.52		
		0.90		

* TPM loss is measured from the weight differences of the Cambridge filter pad placed behind the traps before and after 10 cigarettes were smoked.

** TPM loss (%) was calculated from the TPM of 10 cigarettes (in mg) collected after the water traps divided by the nominal FTC TPM. No correction was made for the pad moisture content.

Figure 4. Total ion chromatograms of total particulate matter from a common commercial Full Flavor filter cigarette: a) regular smoking; b) smoked with two water traps.

Table 8 shows the trapping efficiency of three acids (acetic, formic and lactic).

Further work was done to understand the effect of dilution of the whole smoke solution on the pH. Whole smoke should behave as a buffer solution because it is a mixture of weak acids and weak bases associated with their salts. Experimentally, this buffer character was shown by titrating the whole smoke solution with 0.01 M hydrochloric acid. The theoretical pH variations when adding hydrochloric acid to water or to a buffer solution (of an acid with $pK_a = 5$ and its salt) are shown in Figure 5, while the experimental results for the same titrations are shown in Figure 6. The titration curve for the smoke solution

does not come close to the curve for water at least for the first 2 or 3 mL of titrant. At larger volumes of titrant, the titration curve for smoke was closer to that of water. The experimental pH values do not match perfectly with the theoretical values; but the data were close enough to indicate that, indeed, the aqueous suspension of whole smoke was a buffer. As the general theory for the pH of buffers indicates, this does not vary with dilution (within limits). Therefore the amount of water used in the traps is not critical. This finding is also confirmed by the statement by MARINENKO and KOCH that "in the majority of cases, the pH of a solution cannot be readily reduced to hydrogen ion concentration (acidity) without some

Table 7.
Peak identifications for selected components from the TPM of a commercial cigarette with regular smoking and smoked with two water traps.

Peak no.	Compound	Chemical Abstract no.
1	propylene glycol	57-55-6
2	toluene	108-88-3
3	phenol	108-95-2
4	limonene	138-86-3
5	2-methylphenol	95-48-7
6	4-pyridinol	626-64-2
7	2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	28564-83-2
8	1,3-benzenediol	108-46-3
9	4-methylbenzaldehyde	104-87-0
10	1,4-benzenediol	123-31-9
11	triacetin	102-76-1
12	nicotine	54-11-5
13	myosmine	532-12-7
14	nicotyrine	487-19-4
15	2,2'-bipyridine	336-18-7
16	megastigmatrienone	38818-55-2
17	cotinine	486-56-6
18	neophytadiene	504-96-1
19	hexadecanoic acid	57-10-3
20	phytol	7541-49-3
21	solanesol	13190-97-1
22	hydrocarbon ?	?
23	butyl tetradecanoate	110-36-1
24	butyl hexadecanoate	111-06-8
25	1-dodecene	112-41-4
26	1-tridecene	2437-56-1
27	butyl octadecanoate	123-95-5
28	long chain hydrocarbon	?

Table 8.
Smoke acids in TPM for a commercially available Full Flavor cigarette smoked under regular smoking conditions and with two water traps (values in µg/cig.).

Acid	Regular smoking (µg/cig.)	Smoking with traps (µg/cig.)	Reduction (%)
Formic	29.7	3.6	87.9
Lactic	32.1	11.4	64.5
Acetic	111	2.5	97.7

Chemical Abstract nos. as follows: formic acid, 64-18-6; lactic acid, 50-21-5; acetic acid, 64-19-7.

knowledge of the other ionic components and their concentration in solution as well as understanding of

the systematic errors inherent in the measurement process" (41).

The repeatability of the procedure was initially estimated using a common commercial cigarette that was smoked in triplicate on six different days. The mean smoke pH value was 4.97. The standard deviation did not vary by more than 0.07 pH units. The repeatability evaluation was also done for a 1R4F Kentucky reference cigarette. The mean smoke pH value was 4.62 and the standard deviation was 0.03 pH units. The results are shown in Table 9. The pH values for the water after a blank run in which air was puffed through the water trapping system were 6.63 and 6.47, respectively.

For the evaluation of the influence of vapor phase on the smoke pH value, the smoke for ten 1R4F Kentucky reference cigarettes was collected and the pH was measured after taking 50 clearing puffs. The clearing puffs removed some of the vapor phase from

Figure 5.
Theoretical data for the titration of 100 mL water and of 100 mL buffer (salt/weak acid) solution with 0.01 M HCl).

Figure 6.
Experimental data for the titration of 100 mL water and of 100 mL smoke solution with 0.01 M HCl.

the water solution, but it was not possible to determine if 50 clearing puffs removed completely all the vapor phase components. The results are shown in Table 10. It can be seen that the pH increases with 0.60–0.65 pH units compared to the measurement

Table 10.
pH Values for a 1R4F Kentucky reference cigarette smoked using 50 clearing puffs.

Run	pH Value
1	5.26
2	5.19
3	5.25
Average	5.23 ± 0.01

performed after three clearing puffs. This indicated that vapor phase has a notable contribution to the total pH result, as expected.

In order to investigate whether or not there are any effects of changes in tobacco blends on smoke pH, experimental filter cigarettes made from 100% Burley tobacco (typical 1994 crop) and 100% flue-cured tobacco (typical 1994 crop) were smoked for the pH determination. The data indicated that the smoke from Burley tobacco had a higher smoke pH than flue-cured tobacco (5.4 *vs* 5.0). These data are shown in Table 11. SAKUMA and co-workers have evaluated the levels of particulate-phase acids and bases in flue-cured, Burley, and Oriental tobacco (29, 42). Their data showed that the main difference among the three types of tobacco in terms of particulate phase acids and bases (i.e., excluding ammonia) was that the smoke from the Burley tobacco contained less acetic acid. The data shown in Table 11 are in agreement with these findings. Our findings of only a small difference between the pH of the smoke from an all Burley cigarette and the pH of the smoke from an all flue-cured cigarette is

Table 9.
Repeatability study of smoke pH for a common commercial Full Flavor cigarette and for a 1R4F Kentucky reference cigarette.

Commercial Full Flavor cigarette				1R4F Kentucky reference cigarette			
Day	pH Value			Day	pH Value		
	Run 1	Run 2	Run 3		Run 1	Run 2	Run 3
1	4.93	4.94	4.93	1	4.64	4.65	4.64
2	4.95	4.93	4.94	2	4.63	4.63	4.57
3	4.93	4.95	4.93	3	4.59	4.58	4.57
4	4.91	4.90	4.92				
5	5.10	5.09	5.13				
6	4.97	4.99	4.93				
Average	4.97 ± 0.07			Average	4.62 ± 0.03		

not typical compared to those reported by others. For example, SENSABAUGH and CUNDIFF reported values varying from 6.48 to 7.76 for the pH of the smoke from a 70 mm non-filter cigarette containing uncased Burley tobacco (22). The smoke pH values for an all flue-cured cigarette ranged from 5.66 to 5.89. In GROB's original work on smoke pH (19), he reported a pH of 7.91 for the TPM from Burley tobacco and pH of 4.94 for the TPM from flue-cured tobacco. Neither the technique used by SENSABAUGH and CUNDIFF nor the technique used by GROB fully accounted for the carbon dioxide in smoke. This lack of full accountability for the carbon dioxide caused the wide differences between the smoke pH from an all Burley cigarette and that from an all flue-cured cigarette.

Table 11 also gives the pH values obtained for several commercially available cigarettes including Full Flavor, Lights and Ultra Lights. Except for the relatively low levels of nicotine in the Oriental tobacco, the smoke pH of a typical domestic blend (for example, 30% Burley, 30% flue-cured, 10% Oriental, 10% mixed flue-Burley expanded tobacco, 5% mixed flue-Burley stem, and 10% paper reconstituted tobacco) may well depend on the sugar levels in the flue-cured blend (38) and the amount of sugar used in the Burley casing. This is because the sugars decompose to acidic components on smoking (29). The data given in Table 11

Table 11.
pH Values for several commercial and experimental brands of filter cigarettes.

Brands	pH Value
Full Flavor KS A	4.95
Full Flavor KS B	4.76 4.84
Full Flavor KS C	5.02
Medium KS A (Menthol)	4.91
Medium KS B	4.93 4.80
Medium 100's	5.12 4.93
Ultra Lights KS A	4.88 4.98
Ultra Lights KS B (Menthol)	4.80
Ultra Lights KS C (Menthol)	4.96 4.79
Ultra Lights KS D	5.14
100% Burley	5.43 5.38
100% Flue-cured	5.09 5.01

Figure 7.
Frequency of cigarette brands as a function of smoke pH value.

indicate that for all the studied cigarettes the whole smoke pH was under 5.5 and ranged between 4.6 and 5.5. The standard deviation obtained for these measurements did not exceed 0.15 pH units.

The technique described in this paper was further applied to a wide range of commercially available cigarettes covering 150 brands. Figure 7 shows the frequency of cigarette brands as a function of the pH value.

The correlation between smoke pH and "tar" or TPM levels and nicotine levels was also investigated. Figure 8 shows the plot of TPM values as a function of pH results and Figure 9 shows the plot of nicotine values as a function of pH. No direct relationship was found between the "tar" or TPM and whole smoke pH value, as well as between the nicotine level and whole smoke pH.

A modification of this technique was also evaluated for the possibility to determine puff-by-puff smoke pH. The trapping of one single puff only yields a small amount of smoke and it was questioned if it will provide a meaningful pH value. In order to accumulate more smoke, two consecutive puffs were collected together (one and two, three and four, etc.). Also, the number of cigarettes was increased to 20, and the water volume was reduced to 150 mL. The results for the pH measurement of a commercial Full Flavor cigarette are shown in Table 12. As seen in Table 12, the pH

Table 12.
pH Values for puff-by-puff smoke collection for a commercial cigarette.

Puff no.	pH Value
1 & 2 Puffs	4.93
3 & 4 Puffs	5.08
5 & 6 Puffs	5.06
7 & 8 Puffs	5.07
Whole cigarette smoke	5.02

Figure 8.
Correlation of whole smoke pH with FTC "tar".

values from the first two puffs were slightly lower than those from later puffs. However, for the particular commercial cigarette that was analyzed, little variation was noticed for the pH values of different puffs.

CONCLUSIONS

A new procedure for the determination of smoke pH was established. In this procedure, whole smoke is collected in a series of two water bubble traps, followed by the measurement of the pH in the combined aqueous suspensions from the traps. The procedure includes the contribution from both vapor phase and particulate phase. Whole smoke pH values were

found to have very good repeatability. Data from commercial and experimental cigarettes indicated that the smoke pH values were in a narrow range between 4.6 to 5.5. No direct relationship was found between the "tar" or TPM and the smoke pH values. Also, no direct relationship was found between the nicotine level and the smoke pH values.

During the evaluation of the efficiency of smoke collection, it was found that the absorption of carbon dioxide and TPM was not complete. Depending on the cigarette type (Full Flavor, Lights, or Ultra Lights), the efficiency of the trap varied between 26% to 61% for carbon dioxide, and between 92% to 99% for TPM. The data from this study indicated that the suspension of whole smoke has enough buffer capacity such that

Figure 9.
Correlation of whole smoke pH with FTC nicotine.

variations in the total amount of collected smoke did not significantly affect the smoke pH. The ratio of the absorbed carbon dioxide and absorbed TPM may influence the pH value, while this ratio was found to be constant for a given cigarette.

Also, this technique was modified to determine puff-by-puff pH. Very little variation was noticed for the pH values of different puffs.

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