

**THE CHEMISTRY OF
TOBACCO AND TOBACCO SMOKE**

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Proceedings of the Symposium on the Chemical Composition of Tobacco
and Tobacco Smoke held during the 162nd National Meeting of the American
Chemical Society in Washington, D.C., September 12-17, 1971

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PREFACE

The present volume comprises a compilation of papers presented as a Symposium on the Chemical Composition of Tobacco and Tobacco Smoke during a meeting of the American Chemical Society in Washington, D. C., September 12-17, 1971.

The Symposium was organized so as to cover, in the time allotted, those aspects of tobacco research that are both pertinent and relevant to the most demanding problem facing researchers in the field today--that is the development of a less hazardous cigarette. The path to such an objective, however, is still rather long and not easily traversed.

For example, in identifying the hazard associated with smoking, one must first know something of the chemical composition of tobacco smoke, and moreover, how the smoke components arise from the various leaf components. In addition, bioassays of smoke fractions and components therein are necessary to identify noxious substances, and to correlate biological activity with chemical composition. Finally, to achieve the stated objective, methods need to be developed for removing the identified hazards from the smoke--whether they be by specially cultivating tobacco plants, or by modifying tobacco smoke through the use of filters, additives or similar devices.

The intent of the Symposium was to explore all the above areas. Thus papers were presented which discussed various aspects of the composition of tobacco leaf and how that composition might be altered in the future. In papers on recent findings in the chemical composition of tobacco smoke, methods for fractionating the smoke, and resolving complex mixtures of smoke components by the use of combined capillary column gas chromatography--mass spectrometry were described. Pyrolysis studies which related leaf and smoke components and which attempted to shed light on the mode of origin of smoke components, including those considered to be biologically active, were also taken up by the Symposium. Discussions of methods for bioassaying smoke condensate, and results obtained from utilizing such methods for a number of smoke fractions and identifying the active chemical constituents in these fractions comprised a significant portion of the Symposium. Finally, with all the above as a foundation, the Symposium took

up the question of modifying the smoke and considered in detail the use of various filter systems and additives.

It is hoped, of course, that the Symposium papers, presented in this Volume, will make a contribution, by way of providing pertinent information to research workers in the field, to the objective stated earlier, of current tobacco research.

The editor wishes to thank associates and colleagues who helped, at various times, with the organization and presentation of the Symposium: Dr. R. L. Stedman and Dr. C. F. Woodward who suggested several of the speakers, Dr. J. B. Fishel and Dr. O. T. Chortyk who presided at sessions and all the speakers and participants who contributed their time and knowledge in the field. In addition, the cooperation of Dr. Emily L. Wiek and the other officers of the Agricultural and Food Chemistry Division of the American Chemical Society must be acknowledged.

Irwin Schmeltz

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**THE CHEMISTRY OF
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RECENT TRENDS IN TOBACCO AND TOBACCO SMOKE RESEARCH

Helmut Wakeham

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The excuse for a research director to review before his scientific peers recent progress in the field of his own program does not come often. It is an opportunity not to be missed. In many ways it is more challenging than presenting the program to management who foots the bill. It has the advantage of putting one's own program into better perspective. Any research group tends to become so engrossed in its own work that it overlooks peripheral areas of work -- we see the trees and forget to look at the forest. Frankly, I am not sure my associates have appreciated my involvement in this symposium. In the course of my preparation I have suggested some gaps in our own program which they should be exploring.

In this review I shall refrain from ticking off new compounds recently found in tobacco or smoke, or listing new techniques in analysis and pyrolysis. I shall also not review all the chemical studies being carried out in connection with agricultural and curing investigations on tobacco. I propose rather to view broadly the field of tobacco and smoke chemistry as it pertains to the real life smoking situation. What chemistry is taking place as the smoker puffs away on his smoking product? In laboratories we often do simplified experiments under arbitrary and artificial conditions because it is easier to do things that way. We forget that these conditions may be quite unlike those experienced by human smokers, each of whom is enjoying his pipe or cigaret in different ways from his fellow smokers.

Chemists have been intrigued by the complexity of tobacco and tobacco smoke from the turn of this century. Their interest

arose not only from the widespread use of tobacco, but also from the fact that, except for chewing tobacco, the product of interest is the smoke derived from the combustion of tobacco. Here we have a natural product containing hundreds of chemical constituents exposed to temperatures ranging up to over a thousand degrees Centigrade in the presence of varying amounts of oxygen. Where else, except possibly in complex living organisms, could the chemist find such an inexhaustible supply of chemical problems to keep him forever challenged? Small wonder that the study of tobacco and smoke chemistry has mushroomed even faster than the over-all growth of science.

The first challenge, of course, was analytical. What is in tobacco and smoke to give rise to the pleasurable experience of its use -- the taste, the aroma, the physiological and psychological sensations? Already by 1930 extensive analyses had been made of all categories of substances: alkaloids, carbohydrates, proteins, acids, hydrocarbons, sterols, phenols and polyphenols; (5) (40) and all of this without the sensitive instrumental methods we have today. In fact, it is interesting to note that in their 1959 Chemical Reviews of the "Constituents of Tobacco and Tobacco Smoke" Johnstone and Plimmer (21) were reluctant to accept "isolations and identifications" based on " R_f values, color tests, and ultraviolet spectra" instead of the "criteria of classical organic chemistry." In contrast with this restricted view we now have the sophisticated combined chromatographic, mass spectographic methods. Grob and Vollmin (13), for example, reported after one pass identification of 133 compounds in smoke.

Analysis of tobacco and smoke was, of course, greatly stimulated by the smoking and health controversy. A great search has been made for toxic substances in smoke in attempts to explain the statistical associations with disease. Some analysts with sophisticated methods are now finding chemicals in fractional nanogram quantities, often ignoring the fact that toxicity is a function of concentration. They are looking for the needle in the haystack, as it were, to prevent the cow from eating it.

Consequently tobacco chemists now have compiled a list of some 1350 identified chemical components in tobacco and smoke. Gas chromatographic scans indicate there are many more, probably over ten thousand, possibly even a hundred thousand. Considering the chemical nature of tobacco and the cigaret burning process, we should not be startled by such a prediction. We should rather recognize that simply finding more things in smoke may not be as useful in our quest for applicable knowledge as understanding the nature of the chemical processes involved in growing, curing, processing tobacco and producing pleasurable smoke.

Chemists in the tobacco industry are naturally interested in the smoke generating process. Because tobacco is a product of nature, and because of the tobacco production and marketing system, they have relatively little control of their raw material. Any hope they might have of controlling smoke composition for flavor or other reasons will depend largely on manipulating the cigaret, cigar, or pipe. Apart from filtration, which is another subject, the chemists are more or less limited to the process of converting tobacco into smoke.

It is instructive to take a broad look at the compositions of tobacco and of smoke. Of our 1350 chemical constituents, 440 are reported for tobacco alone, 510 are found in smoke, and about 400 are found in both. (42) It should be noted that many of those substances found only in tobacco or in smoke may simply not have been sought in the other by the investigator. Some we might expect to find in both, some in only one or the other state.

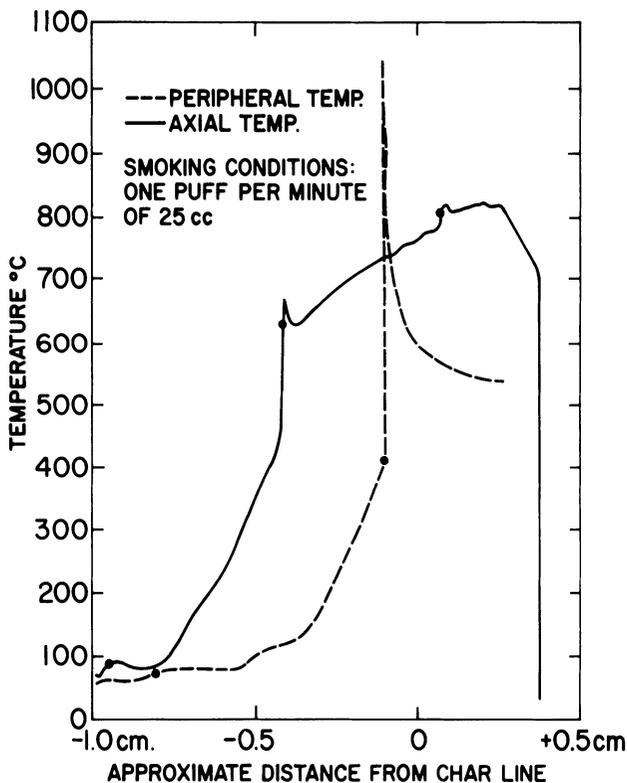


Figure 1. Temperature Profile at Axial and Peripheral Positions Behind the Tip of the Burning Cone.(2) (28)

Let us consider briefly the transfer of chemicals from tobacco to smoke. Those found in both states obviously are being driven from the tobacco into the smoke by the heat of the burning coal. The process involves evaporation and condensation.

Figure 1 charts the increase in temperature of tobacco behind the burning coal in a cigaret as a function of distance.⁽²⁾ (28) It shows how both during puffs and between puffs the tobacco is getting hotter and hotter as the burning zone is approaching. Visual and thermogravimetric observations indicate that even as low as 300°C vapors from the tobacco are condensing to form smoke, at 450°C charring takes place, and around 600°C the tobacco is kindled and starts to burn.⁽³¹⁾ Behind the coal there is a temperature gradient which is very sharp between puffs and less so during the puff when the stream of hot gases from the burning coal passes back through the tobacco rod. Substances which are highly volatile thus are readily distilled from the tobacco behind the hot coal. Less volatile substances being transferred must exhibit adequate vapor pressures and sufficient chemical stability so that the process will take place without chemical modification before evaporation. Let us consider some examples (Table 1).

In this case we would expect about one-third transfer to take place because about that fraction of the tobacco is burning during the puff. We find good transfers for low molecular weight volatile components, less for the higher boiling constituents, least for the large molecules.

Dotriacontane, despite its high boiling point and molecular size, transfers well because it is a stable hydrocarbon.

The presence of larger, higher molecular weight substances in smoke is not clear. Solanesol, which is a C-45 isoprenoid, sterols, sugars, leaf pigments, and even cellulose have all been reported in

Table 1. Tobacco Chemicals Transferred to Mainstream Smoke.

<u>COMPOUND</u>	<u>BP</u>	<u>% TRANSFER (APPROX.)*</u>
Menthol	212° C	39
Nicotine	245° C	24
Glycerol	d.290° C	22
Neophytadiene	284° C	20
Nornicotine	270° C	8
Dotriacontane	467° C	30
Solanesol (M.P.)	41.5° C	3

* BASED ON CONTENT IN TOBACCO CONSUMED

Table 2. Some Types of Compounds Found in Tobacco Smoke.

Aliphatic Hydrocarbons	Naphthols
Aromatic Hydrocarbons	Nitro Compounds
Carbazoles	Nitriles
Many Esters	Piperidines
Furans	Pyrazines
Fluorenes	Pyrrolidines
Indans	Toluidines
Indoles	

smoke. Certain low molecular decomposable substances like amino acids have also been found. The presence of all these has been explained by the hypothesis that under thermal stress the tobacco cells "explode" and eject into the stream involatile solids. One must also remember that, especially with non-filter cigarets, tobacco particles are often swept into the smoke collection devices during the puff. In both of these ways unexpected involatile substances could show up in a smoke condensate analysis. Starch, proteins, pectins, chlorophyll and the like have not been identified in smoke and would, in general, not be expected there.

Finally, there are also in smoke the products of pyrolysis, oxidation, and high temperature synthesis. Some examples of these are shown in Table 2.

These and other "new" substances which are the result of reactions occurring during smoking represent a large part of the 900 identified constituents in smoke. The chemistry of their

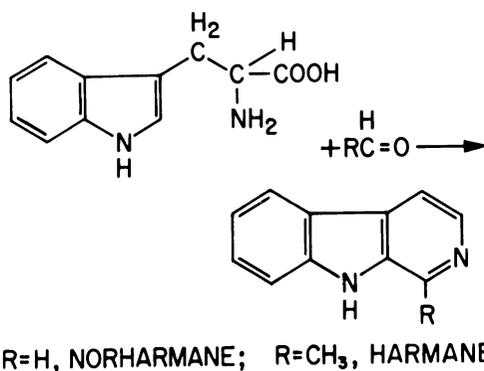


Figure 2. Formation of Harmanes from Tryptophan and Aldehydes.

Table 3. Tryptophan to Harmanes Conversion in the Cigarette. (34) (35)

A. Radiotracer Experiment

169 nci ^{14}C -Tryptophan added per cigarette

	YIELD	
	<u>NORHARMANE</u>	<u>HARMANE</u>
Activity in Smoke	0.80 nci	0.26 nci
% Conversion	0.47	0.15

B. Tobacco Loading Experiment

Control Yield	11.2 μg	4.3 μg
Added 820/ μg Tryptophan/Cigarette		
Observed	15.7 μg	5.9 μg
Increase	4.5	1.6
Predicted	3.9	1.2

formation is naturally a subject of great interest to the tobacco chemist. Accordingly, we find an increasing number of investigators looking into the question of what and how tobacco constituents are precursors of chemicals formed during the burning process.

Three different approaches have been employed. In the first, tobacco has been loaded or spiked with the suspected precursor and smoked. The smoke is then analyzed for increases in amounts of the suspected products. Here are some examples of this technique (Fig. 2, Table 3, Fig. 3):

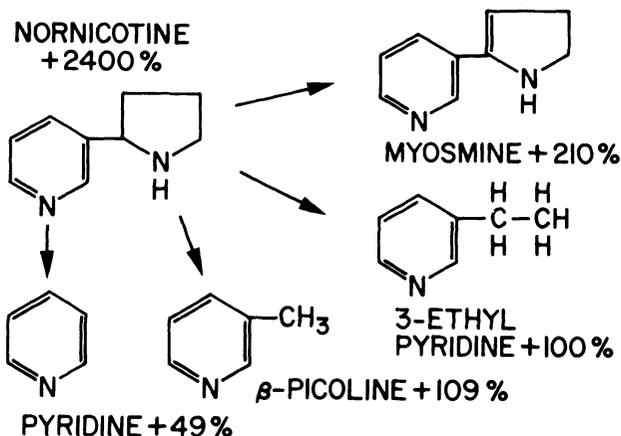


Figure 3. Effect of Nornicotine Addition. (11)

The first example (Fig. 2) involves the conversion of the amino acid tryptophan to the carbolines harmane and norharmane by reaction with an aldehyde.⁽³⁴⁾⁽³⁵⁾ Tryptophan is present in tobacco either as an amino acid or as a component of tobacco protein. In a second experiment (Table 3) 820 µg/cigt of tryptophan added to the tobacco gave an increase in norharmane and harmane yields about as expected from the radiotracer data.

Another example (Fig. 3) involves the addition of nornicotine, the demethylated nicotine analog.⁽¹¹⁾ A 24-fold increase of nornicotine produced the indicated increases in the nitrogen bases which might be expected as breakdown products from nornicotine. One of the problems in this type of experiment is that the added precursor is probably not located in the tobacco in the same way as the naturally occurring one. As the thermal stress develops the evaporation and/or pyrolysis may not be the same for the added component as for the natural one. The breakdown products might also be different. Another difficulty with this type of experiment is that substantial loading of the tobacco with the precursor in question may change the burning properties of the tobacco.

A second approach to the problem of identifying precursors has been to pyrolyze in a hot tube or furnace individual precursor candidates and to analyze the pyrolysis products. This technique is useful for indicating what compounds might be looked for in the more sophisticated radiotracer experiments; or, conversely, it may also be used to identify many precursors for a given smoke constituent.

For example (Table 4), many substances when pyrolyzed yield benzo(a)pyrene.^{(24) (12) (36)}

Table 4. Benzo(a)pyrene in Pyrolysis Products.⁽²⁴⁾

<u>PRECURSORS</u>	<u>µg B(a)P FROM 100G OF STARTING MATERIAL</u>
Triethylene Glycol	3
Glycerol	6
Sorbitol	13
Starch	7
Cellulose	8
Hydroxyethyl Cellulose	34
Gum Arabic	32
Agar - Agar	47

Obviously, to pinpoint a specific precursor in tobacco would be a futile exercise. A similar situation exists with the occurrence of phenol in smoke (Table 5).

Bell and co-workers (4) pyrolyzed various carbohydrates in air and nitrogen to show that many form phenol at elevated temperatures. It is interesting to note that higher phenol yields are obtained in the absence of air with its competing oxidation reactions (Table 5).

The more extensive analysis of pyrolysis products from malic acid is illustrated in Table 6.

Here only the presence or absence of products are indicated. It is interesting to observe that at higher temperatures the lower weight oxygenated products give way to polynuclear hydrocarbons. Thus, we obtain by this method not only scope of the pyrolysis products, but also clues regarding their temperatures of formation and thermal stability.

Pyrolysis experiments do give some information about thermal conversions of tobacco constituents into smoke chemicals. The problem arises in the interpretations of the results. Pyrolysis conditions only approximate the burning cigaret and make no allowance for the presence of other tobacco components.

This leads us to the third general technique of studying precursors -- that employing labeled compounds. Here we may use either radioactive or mass isotopes. The radioactively labeled compounds can be added to tobacco in extremely small quantities without interfering with the normal burning characteristics of the tobacco.

Uniformly labeled radioactive ^{14}C -glucose and ^{14}C -sucrose were applied to cigaret tobacco by Gager and co-workers (8) (9) and by Thornton and Valentine. (45) The cigalets were smoked with the results shown in Table 7.

Similar results were obtained with sucrose. Note that over half of the combustion products appear in sidestream smoke and that a wide variety of radioactive oxidation and pyrolysis products were identified. Of particular interest is the presence of radioactive acetonitrile which would not have been found in a pure compound pyrolysis experiment. It must have been formed by reaction with nitrogenous compounds in the tobacco. Another point is of interest in connection with our earlier remarks about entrainment in the smoke stream. Gager and co-workers report 0.5% of the original radioactive sugar in the mainstream particulate smoke.

So far we have considered the general field of tobacco smoke

Table 5. Pyrolysis of Carbohydrates to Phenol.⁽⁴⁾

<u>PRECURSOR</u>	<u>100 (% CONVERSION)</u>	
	<u>IN AIR</u>	<u>IN N₂</u>
Glucose	5.0	9.0
Sucrose	6.7	8.2
Starch	0.2	10.0
Cellulose	2.4	4.0
Pectin	2.6	3.9
Rutin	0.8	2.8

MAX. TEMP. 685°C; GAS FLOW 100 ml/min.

Table 6. Products from Pyrolysis of Malic Acid Observed at Various Temperatures.⁽¹⁰⁾

	<u>500°</u>	<u>600°</u>	<u>700°</u>	<u>800°</u>	<u>900°C</u>
Benzene	+	+	+	+	+
Toluene	+	+	+	+	+
Indene	+	+	+	+	+
Biphenyl			+	+	+
Naphthalene			+	+	+
Ethylbenzene } m-,p-Xylene }			+	+	+
Styrene } o-Styrene }			+	+	+
Dimethylnaphthalene					+
Acenaphthylene				+	+
Anthracene (Phenanthrene)				+	+
Fluorene				+	+
Pyrene					+
Chrysene					+
Phenol	+	+	+		
m-Cresol	+	+	+		
p-Cresol	+	+	+	+	
o-Cresol	+	+	+	+	
2,5-Xylenol		+	+	+	
Fumaric Acid	+	+	+		
Succinic Acid	+	+			+

Table 7. Distribution of Products from ^{14}C -Glucose in Tobacco.(8)(9)

	<u>% TOTAL ACTIVITY</u>
Butt	41
Sidestream Smoke	51
Mainstream Smoke	
Particulate	1.7
CO ₂	2.7
Other Gases*	2.0
<hr/>	
* Identified Compounds Include	
Acetaldehyde	2-Butanone
Acetone	2-Buten-2-One
Acetonitrile	
Acrolein	2,3-Butanedione
Benzene	Crotonaldehyde
Furan	2,5-Dimethylfuran
2-Methylfuran	Propionaldehyde

chemistry in a more or less traditional way. To go further into the subject it will be useful at this point to consider the reaction conditions in the burning zone in considerably greater detail than heretofore. We will for the sake of simplicity limit ourselves to the cigaret (Fig. 4), although much of what has already been said applies to pipe and cigar smoking as well.

Smoke is produced by the smoker puffing through the cigaret and by smoldering between puffs. The two smokes, identified as mainstream and sidestream smokes, are not the same. Both streams are composed of particulate phase and a gas phase, generally defined as that portion not removed by the conventional Cambridge filter.

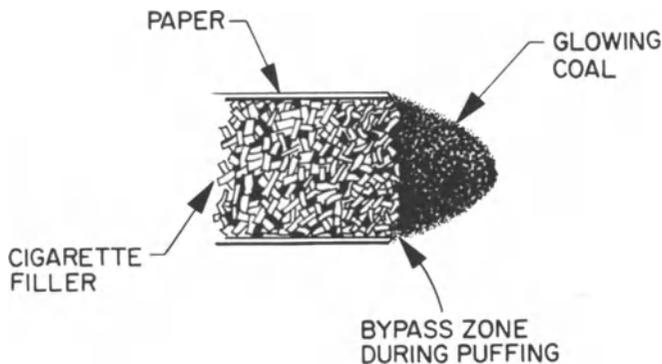


Fig. 4. Longitudinal Section of the Burning Cigaret.

After the cigaret is lit and allowed to smolder a bit, a burning cone appears at the ignited end (Fig. 4). This cone has a higher density of material than the tobacco behind it, produced by coking and swelling of the tobacco shreds and by the recondensation of evaporation and pyrolysis products induced by the smoldering process itself. One manifestation of this dense cone is an increase in the resistance to draw of the overall cigaret, a reduced permeability to air. At the same time the porosity and burning rate of the cigaret paper tends to keep the periphery of the cone unobstructed. In fact, the paper burns away ahead of the tobacco to a point where further burning is halted by the quenching effect of air flow to the burning cone from behind.

Now comes the puff, drawing air past the burning coal around the periphery of the cigaret. This flow provides more oxygen to this area and increases its maximum temperature, much like a blacksmith blowing air on his charcoal to increase the temperature of his forge. The hot gases from this zone, drawn into the cigaret, again swell the tobacco filaments behind the cone and reduce the airflow. The combustion zone is still further bypassed, with the result that for very strong puffs, the volume of cigaret consumed is actually less than for weaker puffs. (14) During the puff, then, the shape of the burning cone is distorted from its natural smoldering shape. This shape is gradually restored during the interval between puffs.

In the swelling of and condensing on the tobacco behind the burning zone during the puff, the otherwise normal flow of oxygen to the backside of the cone is reduced. (7) (14) (41) This "choking" off of the oxygen persists for a time after the puff with the result that the rate of tobacco consumption is actually lower than for the natural smoldering process. This fact is borne out by the observation of an increase in smoldering temperature some time after the puff, usually about forty seconds into the interval. The normal oxygen supply is now restored.

The maximum temperature for the burning tobacco, periphery or coal will fluctuate as shown in Fig. 5 for puffs and between puffs. (26)

Oxygen availability to the burning zones will likewise vary. Both temperature and oxygen will then depend on the velocity of the air stream during puffing, the duration of the puff, the interval between puffs, and the density of the tobacco rod and coal as they affect heat transfer and radiation and convection losses. It is clear from these considerations that the chemistry of the smoke will vary (1) between mainstream and sidestream smoke for a given puff condition and (2) among various puff conditions.

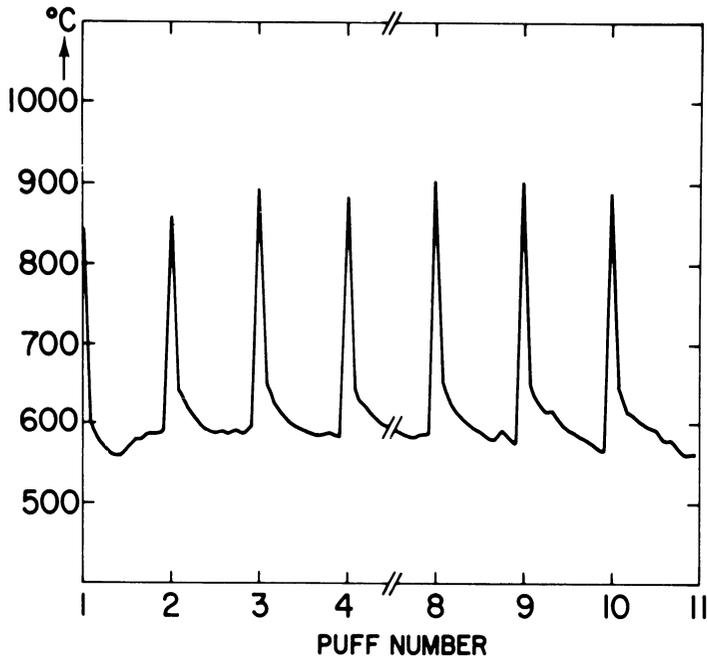


Fig. 5. Temperature Scan of Burning Region Showing Maximum Values. (26)

We need, therefore, a standard puff condition for chemical studies of the cigaret. As most of you know, this has been established for the Federal Trade Commission test on tar and nicotine. (33) The test involves a 35 ml volume puff of two seconds duration once a minute. This test condition is an arbitrary choice based on a consideration of how the "average" smoker puffs his cigaret.

It should be stressed that smokers may vary widely from this standard smoking pattern. (1) (22) The observed ranges are shown in Table 8 for a number of smoking parameters.

Note that flow rates for air drawn into the cigaret during the puff by different people exhibit a 1 to 10 ratio for the lowest

Table 8. How Smokers Puff Cigaretts.

<u>PUFF</u>	<u>LOWEST</u>	<u>STANDARD</u>	<u>HIGHEST</u>
Volume ml	17.0	35.0	73.0
Duration Sec.	0.9	2.0	3.2
Rate ml/Sec.	5.6	17.5	81.0
Interval Sec.	22.0	60.0	72.0