Tobacco Products and Smoke

General Report*

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This is a general report about the work done in the fields of tobacco and smoke chemistry and physics during the time since the last congress in Salisbury in 1963 and it deals with a great many important and very interesting papers on the subject mentioned in this short period.

Ten years ago, or even less, people smiled — in Europe at least — at a chemist or a physicist intending to join the tobacco industry. The papers published on tobacco chemistry were at that time restricted to methods which were common in the field of food chemistry and were of general applicability only on closely related subjects. During the following years, however, a remarkable revival of tobacco and tobacco smoke chemistry was noted, and now — particularly during the last years — an obviously stimulating effect can be observed to radiate from tobacco and especially smoke chemistry to other fields of analytical chemistry. At least this is noticeable in the area of microanalysis.

It is almost the normal case in tobacco and smoke chemistry that constituents of interest occur in the ppm-range of concentration and moreover smoke is of an extraordinary complexity scarcely observed in other fields. Furthermore it is certainly much more difficult to obtain large quantities of tobacco smoke for analytical operations than of other products. In order to investigate the composition of coal tar one could start with tons of material, whereas the analysis of tobacco smoke is normally started with grammes; 50,000 cigarettes normally yield 1 kilogramme of total particulate matter.

For these reasons the solution of our problems needs sophisticated methods of microanalysis.

Several of these methods, developed for smoke and tobacco, are therefore of general interest and even solve problems in other fields of research. For instance the gas chromatographic technique developed by *Grob* (1, 2, 3) during the last few years, using glass capillary tubes which can be coated by coherent films of polar liquids, if first covered by carbon black, has a degree of separation capability never reached before. *Grob* (4) reached a number of 360,000 theoretical plates. The method was developed for the separation of the gaseous phase of tobacco smoke. The combination of this type of gas chromatography and mass spectrometry published by the same author (5) very recently represents a separation and identification method with a remarkable degree of perfection. A different method developed by *Grob* (6) is of general applicability for the separation of amines by gas liquid chromatography. The liquid phases proposed by the author: polyethylene-imine and polypropylene-imine are the first reported to allow the separation of primary and secondary amines by gas chromatography. The isolation technique for the separation of polycyclic aromatic hydrocarbons by means of nitromethane and subsequent column chromatography first published by *Grimmer* (7, 8) — thus permitting the simultaneous determination of up to 13 hydrocarbons — was developed on tobacco smoke. It found a very widespread application in food and air pollution as well as petroleum chemistry. Other analytical tools developed for tobacco and smoke research are the coloured and crystalline 4-nitroazobenzene-(4')-carboxamides (9) for the identification and separation of primary and secondary amines and the 5-nitro-2-hydroxybenzal (10) derivatives of asymmetric hydrazines used for the identification and separation of N-nitroso compounds, which, for instance, met with interest in the field of rocket fuels.

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FIGURE 1
 α - and β -4,8,13-Duvatriene-1,3-diol

FIGURE 2
Cembrene

FIGURE 3
 α - and β -3,8,13-Duvatriene-1,5-diol

FIGURE 4
 α -5,8-Oxido-3,9,13-duvatrien-1-ol

FIGURE 5
 α - and β -5,8-Oxido-3,9(17),13-duvatrien-1-ol

FIGURE 6
Solanone:
L-(+)-2-Methyl-5-isopropyl-1,3-nonadien-8-one

FIGURE 7
4,8-Dimethyl-6,8-dihydroxy-11-isopropyl-14-keto-4,9-pentadecadienoic acid

FIGURE 9
 α_2 -Levantanolide

Last but not least, the isolation and structure elucidation of the 14-C membered ring structures of the duvane compounds performed in 1962 by *Roberts and Rowland* (11) represent some progress in the field of the chemistry of natural compounds as well as the 13-C ketone solanone which was found by *Johnson and Nicholson* (12) in 1965.

These examples are suitable to throw light on the status of tobacco and smoke chemistry today. The difficulties we have to overcome daily in our field will be a good basis which will necessarily produce new and sophisticated methods useful not only in our domain but also of general interest. During the last three years a large number of analytical and physical methods of tobacco and smoke chemistry have been developed. It was not possible to treat all subjects and papers published during this period. Certainly there are even important papers which will remain untreated in this report because of the enormous number of contributions all over the world. Some additional information is given in the following figures and tables, which will render this review somewhat more complete.

TOBACCO CHEMISTRY

It was in 1962 that *Roberts and Rowland* published their first paper on the isolation and identification of macrocyclic diterpenes, the ground structure of which they called "duvane" from the Serbian "duvan" for tobacco. The first pair of isolated substances were 14-C membered ring diols as in Figure 1.

Concurrently a 14-C membered unsaturated hydrocarbon cembrene (Fig. 2) was isolated from "Pinus albicaulis" (13).

It has been shown to contain an identical ring system. Later on *Rowland and Roberts* (14) isolated two further allylic isomers (Fig. 3) and in 1964 the *Reynolds* people isolated from tobacco and smoke three ethers derived from the duvatrien system (15) (Fig. 4 and 5).

A terpenoid 13-C ketone was isolated by *Johnson and Nicholson* (12) in 1965 from tobacco, and called "solanone" (Fig. 6).

A pair of diastereoisomers of precursors for solanone were isolated by *Kinzer and Page* in 1965 (16). The structure (Fig. 7) of these compounds can be brought into relationship with the duvatrienes mentioned just before if an oxidative cleavage of the double bond between C₈ and C₉ is taken to exist (Fig. 8).

In 1962 *Giles, Schumacher, and Young* (17) isolated a new saturated diterpene lactone from Turkish tobacco which was identified as α_2 -levantanolide (Fig. 9). Like the previously described α - and β -levantenolides (18) it belongs to the labdane series and was found to be the second to have the 13-epi configuration.

A great number of newly isolated tobacco constituents comprising carbonyl compounds, acids, amines, and polyphenols can be seen from Table 1.

Some interesting studies should be mentioned here, such as the paper by *Chakraborty and Weybrew* (19) on the chemistry of tobacco trichomes which was published in 1963 and the paper by *Mold, Means, and Ruth* (32) on the higher fatty acids of flue cured tobacco and the finding of cyclohexyl substituted acids in 1965.

In 1964 *de la Burde, Poindexter, and Bell* (33) found the qualitative composition of free amino acids to be similar in all types of tobacco. The types only differed in the quantitative patterns.

A study of the factors affecting the levels of nitrate nitrogen in cured tobacco leaves was carried out by *Broaddus, York, and Moseley* (34) in 1965. The authors found environmental influences to be the most relevant factors affecting the levels of nitrate nitrogen.

In 1963 *Mold, Stevens, Means, and Ruth* (35) established the presence of homologous 2-methyl and 3-methyl-paraffins ("iso" and "anteiso" paraffins) in tobacco. The authors found the homologues with odd C-atom numbers predominating for the normal and the 2-methyl series. In the case of the 3-methyl series, the members with even C-atom numbers are the major components. In the normal and the iso series the C₃₁ compound is the most abundant, whereas in the anteiso series the hydrocarbon with C₃₂ was present to the largest amount.

During our sessions in Athens we learned from *Carugno and Rossi* (36) that branched paraffins can advantageously be separated from normal paraffins by use of glass capillary columns in gas chromatography. The authors found evidence of the occurrence of hydrocarbons with probably 40 and 41 C-atoms in tobacco smoke. *Pyriki* (37) found 90% of the paraffins to possess between 26 and 32 C-atoms and to be mostly straight chained.

In 1964 *Wright, Burton, and Berry* (38) separated 3 pigments present in the dialysable fraction of leaf extracts by gel filtration. The main pigment was a polymeric iron protein-chlorogenic acid complex with a molecular weight of 4,000.

TABLE I

Further new tobacco constituents*

Constituent	Authors	Year
Methylpropylketone	Chakraborty and Weybrew (19)	1963
Methylisopropylketone		
5-Hydroxymethylfurfural	de la Burde, Crayton, and Bavley (20)	1964
m-Tolualdehyde	Burdick, Schmeltz, Miller, and Stedman (21)	1963
Undecyl acetate	Chakraborty and Weybrew (19)	1963
Benzylacetate	Burdick, Schmeltz, Miller, and Stedman (21)	1963
Butyric acid	Kaburaki and Sato (22)	1962
Caproic acid		
Heptylic acid		
Caprylic acid	Schmeltz, Miller, and Stedman (23)	1963
Pelargonic acid		
Methylethylacetic acid	Kaburaki and Sato (22)	1962
Isocaproic acid	Schmeltz, Miller, and Stedman (23)	1963
Azelaic acid		
2-Isopropylmalic acid	Fukuzumi, Takahara, Kaneko, and Onishi (24)	1965
2-Furoic acid	Kaburaki and Sato (22)	1962
D- β -Phenyllactic acid		
p-Hydroxyphenylacetic acid	Fukuzumi, Takahara, Kaneko, and Onishi (24)	1965
p-Hydroxycinnamic acid		
Protocatechuic acid		
2-Pyrrolidine acetic acid	Tomita, Mitusaki, and Tamaki (25)	1964
1-Pipecolic acid		
Indoleacetic acid	Sirois (26)	1963
Arginine	Pyriki and Müller (27)	1963
Ethylamine	Neurath, Krull, Pirmann, and Wandrey (28)	1966
iso-Propylamine		
iso-Butylamine	Yasumatsu and Akaiki (29)	1965
Phenethylamine		
Methylethylamine		
Methyl-n-propylamine	Neurath, Krull, Pirmann, and Wandrey (28)	1966
Methyl-phenethylamine		
1,2,5,6-Tetrahydropyridine		
Aniline		
4-O-Caffeoylquinic acid		
3-Feruloylquinic acid	Zane, Steck, and Wender (30)	1965
1-O-Caffeoylglucose		
1-O-Feruloylglucose		
Astragalin		
(Kaempferol-3-glucoside)		
Rutin-7-glucoside	Watanabe and Wender (31)	1965
Nictoflorin		
Nictoflorin-7-glucoside		

* supplementary to the text

A lot of work has also been done on the composition of tobacco smoke. In a paper which *Caroff, Veron, Badre, and Guillerm* (39) published in 1964, they described how 25 hydrocarbons from C_1 to C_6 were identified by means of a gas liquid chromatography technique utilizing hexadecane and dimethylsulfolan as liquid phases and flame ionization detection. In comprehensive studies *Johnstone, Entwistle, and Dare* (40) investigated the long chain olefines and polyolefines of tobacco smoke. They identified the following homologous series: $CH_3(CH_2)_nCH=CH_2$ ($n = 7 - 25$); *cis/trans*- $CH_3(CH_2)_nCH=CH \cdot CH_3$ ($n = 9 - 28$); *cis/trans*-(CH_3) $_2CH(CH_2)_nCH=CH \cdot CH_3$ ($n = 7 - 26$); *cis/trans*- $C_2H_5(CH_3)CH(CH_2)_nCH=CH \cdot CH_3$ ($n = 6 - 25$); (CH_3) $_2C=CH(CH_2)_nCH_3$ ($n = 8 - 27$); $CH_2=C(CH_3)(CH_2)_nCH_3$ ($n = 9 - 28$). The authors found no alteration between odd and even numbered members of the homologous series.

Since they found no evidence for the occurrence of these olefines in tobacco, they concluded the mentioned compounds to be products of pyrolysis. In a recent paper (41) the authors described the presence of polymethyl-polyolefines, for instance 3,7,11,15,19-pentamethyl-eicosa-2,6,10,14,18-pentaene, in all *trans*-configurations, which are absent in green or cured tobacco, thus indicating them to be formed in the course of pyrolysis. Interesting is the occurrence of 2,4-dimethyl-4-vinyl-cyclohexene (Fig. 10) which was identified by *Cook, Johnstone, and Quan* (42) as well as the occurrence of the tetrahydro-trimethylnaphthalene ionene (Fig. 11) identified by *Edmunds and Johnstone* (43) in tobacco smoke in 1965. These compounds throw some light on intermediates of pyrolytic reactions which lead finally to naphthalene compounds, which were identified in the condensate of 25,000 cigarettes by *Cook, Johnstone, and Quan* (42) in 1963. The following Table 2 gives the yields in microgrammes per cigarette.

In 1964 *Osman and Barson* (44) determined the low boiling aromatic hydrocarbons in cigar smoke.

As to carbonyl compounds, *Rodgman and Cook* (45) in 1965 could identify hexahydrofarnesylacetone, the so-called Phytol (Fig. 12) in Turkish tobacco smoke as well as solanone and a lot of phytylesters of saturated and unsaturated long chain fatty acid from C_{11} to C_{18} .

The phenol compounds of tobacco smoke were studied in several papers most of which are listed in Table 3 showing new smoke constituents.

FIGURE 10

2,4-Dimethyl-4-vinyl-cyclohexene

FIGURE 11

Ionene:
1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene

FIGURE 12

Hexahydrofarnesylacetone

TABLE 2
Naphthalene compounds in cigarette smoke (42)

Substance	Yield (μ g/cigarette)
Naphthalene	0.17
2-Methylnaphthalene	0.50
1-Methylnaphthalene	0.50
2,7-Dimethylnaphthalene	0.26
2,6-Dimethylnaphthalene	0.26
1,6-Dimethylnaphthalene	1.30
1,3,6-Trimethylnaphthalene	0.70
Phenanthrene	0.10
Fluoranthene	0.08

TABLE 3

Further new tobacco smoke constituents*

Constituent	Authors	Year
Ethylbenzene Ethyltoluenes o-Xylene p-Cymene Indene	Cook, Johnstone, and Quan (42)	1963
Pyrogallol-1,3-dimethylether	Kato et al. (46)	1963
Eugenol iso-Eugenol	Rodgman and Cook (47)	1964
Myristicin	Schmeltz, Stedman, Ard, and Chamberlain (48)	1966
p-Hydroxybenzaldehyde m-Hydroxybenzaldehyde Vanillin Syringaldehyde Protocatechualdehyde 5-Hydroxymethyl-furfural	Yang and Wender (49)	1964
p-Hydroxybenzoic acid m-Hydroxybenzoic acid o-Hydroxyphenyl acetic acid m-Hydroxyphenyl acetic acid p-Hydroxyphenyl acetic acid Vanillic acid Syringic acid Protocatechuic acid p-Coumaric acid Ferulic acid p-Hydroxyphenylpropionic acid m-Hydroxyphenylpropionic acid	Yang and Wender (50)	1962
Salicylic acid iso-Vanillic acid Chlorogenic acid Neochlorogenic acid	Steck, Yang, and Wender (51)	1965
	Steck and Wender (52)	1965
n-Propylamine n-Butylamine iso-Butylamine iso-Pentylamine Phenethylamine Methylethylamine Diethylamine Methyl phenethylamine Aniline	Neurath, Dünger, Gewe, Lüttich, and Wichern (53)	1966
Piperidine Pyrrolidine 2-Methylpyrrolidine 1,2,5,6-Tetrahydropyridine	Neurath, Pirmann, and Dünger (54)	1965
	Neurath, Dünger, Gewe, Lüttich, and Wichern (53)	1966
3-Ethylpyridine 3-Vinylpyridine 3,5-Lutidine 3-Acetylpyridine 3-Methylaminopyridine Dihydrometanicotine	Yamashita, Kobashi, and Watanabe (55)	1963
	Osman and Barson (56)	1964
	Neurath, Dünger, Gewe, Lüttich, and Wichern (53)	1966

* supplementary to the text

TABLE 3 (Forts.)

Constituent	Authors	Year
Quinoline iso-Quinoline Pyrazine 2-Methylpyrazine 2,6-Dimethylpyrazine Quinoxaline Pyrrolo(2,3)pyridine Pyrido(2,3)indole	Testa and Testa (57)	1965
Acetonitrile Propionitrile Butyronitrile iso-Butyronitrile Valeronitrile iso-Valeronitrile Capronitrile iso-Capronitrile	Campbell, Rhoades, and Gross (58)	1963
	Grob (3)	1965
Furfurylalcohol	Guvernator (59)	1963

In 1964 *Smith and King* (60) performed an interesting gas chromatographic separation of phenols as methyl ethers or acetates, using a stainless steel capillary coated with 2,4-xylenyl phosphate with excellent resolution properties and succeeded in identifying 2,3-xylenol in addition to the known phenols of tobacco smoke.

As to the bases of tobacco smoke, a lot of work has been done, mostly concerning the pyridine bases which can be handled easily by gas chromatography; *Osman and Barson* (56) isolated 16 pyridine bases from cigar smoke. Among them, 3,5-lutidine and 3-acetylpyridine were newly identified. Pyridine was the major component with 170–218 µg/cigar. Another paper on this subject, but with cigarette smoke, was published by *Schmeltz, Stedman, Chamberlain, and Burdick* (61), also in 1964, thus confirming the results of *Osman and Barson*.

Rodgman and Cook (62), in 1962, were the first to identify indole, 3-methylindole, dimethylindoles, and trimethylindoles, carbazole, methyl-carbazoles, and pyrocoll in microgramme amounts in the cigarette smoke of Turkish tobacco. This work was followed up more recently by several papers from different authors; *Schmeltz, Stedman, Chamberlain, and Stills* (63) in 1965 published a paper on the same subject with additional identification of benzyl-benzoate, and in France the *Testas* (64) performed a quantitative determination of heterocyclic nitrogen compounds in 1964. A paper by *Poindexter et al.* (65) on the occurrence of harmans should be mentioned again. In 1963 *Yamashita, Kobashi, and Watanabe* (55) reported on 3-ethyl- and 3-vinyl-pyridine as constituents of cigarette smoke, which they later found to be thermal degradation products of nicotine. In recent papers our own group (53) reported on the occurrence of, for instance, dihydrometanicotine, 3-methylaminopyridine, 1,2,5,6-tetrahydropyridine, and several amines as well as N-nitroso-dimethylamine and N-nitroso-pyrrolidine (66) in very small traces in tobacco smoke, while *Serfontein and Hurter* (67) reported on the additional occurrence of N-nitroso-piperidine and N-nitroso-diethylamine in tobacco smoke as well. A very interesting point is the occurrence of nitriles in tobacco smoke, which was first reported in 1963 by *Campbell, Rhoades, and Gross* (58), who detected acetonitrile, and extended by *Grob* (3), in 1965, who found the homologues up to capronitrile. Another interesting point is the isolation of a glycoside mixture of sterols containing stigmasterole, sitosterole, and campesterole from smoke, which was published by *Kallianos and Shelbourne* (68) in 1963 and, on the other hand, the identification of polyphenols as chlorogenic and neochlorogenic acids by *Steck and Wender* (52) in 1965.

During the period reported on, growing interest in the composition of the gas phase of tobacco smoke could be observed. The various contributions by *Grob* (1, 2, 3, 5), as mentioned earlier, comprise gas chromatographic techniques which led to a very high degree of resolution. Many of

the identifications of gas phase constituents could be completed by retention values and comparison with authentic samples. In a very recent publication the author used the combination between high resolution gas chromatography and mass spectrometric identification of the substances. *Grob* succeeded in the identification of 84 substances out of the 167 compounds registered (5). Another 12 substances could be identified with high probability. 32 molecular formulae and 39 molecular weights were determined. *Grob* concluded that hardly any components which are relevant from their amount could have remained undetected.

In 1965 *Newsome, Norman, and Keith* (69) estimated the concentration of 80 gaseous components of the tobacco smoke. In the same year, *Norman and Keith* (70) stated the important fact that essentially all N-oxides in fresh, normally obtained cigarette smoke are nitric oxide, and nitrogen dioxide is present at the most in trace quantities only. They are formed almost exclusively from nitrate as found by our own group (71) and *Broadbush, York, and Moseley* (34). Another noteworthy result is the identification of methylisocyanate in cigarette smoke by *Philippe and Honeycutt* (72) in 1965; its amount was estimated by IR-method at 0.2 to 0.8 µg/puff.

REVIEWS

At the end of these chapters a few references should be made to reviews on some subjects. A review on the occurrence of aromatic hydrocarbons in tobacco smoke was given by *Elmenhorst and Reckzeh* (73) in 1964, and a review on phenols in tobacco and smoke by *Herrmann* (74) appeared in the same number of "Beiträge zur Tabakforschung". Under the title "Chemical Studies on Tobacco and its Smoke" a review was published by *Quin* (75) in "Selecta Chimica", and a paper on "Tobacco Alkaloids and their Pyrolysis Products in Smoke" was written by *Kuhn* (76) in 1965. Last but not least a paper was written by *Wynder and Hoffmann* (77) from the chemical as well as biological point of view.

Pyrolysis

Very informative papers have appeared concerning pyrolysis.

Cook, Johnstone, and Quan (42) concluded that the aforementioned 2,4-dimethyl-4-vinyl-cyclohexene and dipentene mainly arise from the thermal degradation of long chain olefinic terpenes as, for instance, solanesol, because the aromatic hydrocarbons which originate from them, namely m-xylene, ethyl-toluenes, and trimethyl-benzenes as well as p-cymene and p-isopropenyltoluene, do not occur in smoke from tobaccos previously extracted.

Conversely benzene and toluene do occur in the smoke of extracted tobaccos, and therefore it is probable that they derive from lignin and peptides. The authors ascribed the occurrence of fluorene and fluoranthene to a Diels-Alder-reaction starting from indene and acenaphthylene respectively and butadiene. The dimerisation of isoprene contributes to the origin of dipentene to a lesser extent.

In 1965 *Edmunds and Johnstone* (43) studied the pyrolysis of β-carotene and found ionene to be the main product, which was mentioned earlier as smoke constituent.

In 1963 *Kobashi, Hoshaku, and Watanabe* (78) studied the air stream pyrolysis of nicotine. The first attack takes place on the N-methyl-pyrrolidine ring. At 300° to 350° C myosmine is formed, which is cleft at 400° C to 3-vinylpyridine and 3-cyanopyridine. At higher temperatures scission of the pyridine ring occurs.

As to the smoking process of cigarettes, the importance was attached to selectivity problems in general. A discussion of the Smoke Study Group of CORESTA* held in Pully in 1965 led to new definitions for the description of phenomena (79) in the burning process of a cigarette and the distribution of the total smoke to the different smoke streams which escape at different points on the cigarette (80).

To give an exact picture of the burning process in the glowing cone of a cigarette it would be necessary to trap the total smoke formed during the process. That means trapping of not only the main stream but also the side stream smoke is necessary to obtain a balance of a component.

A certain amount of burnt tobacco can deliver different amounts of a certain component into the sum of all smoke streams. Therefore it was proposed to talk about "total yield" of a component. Firstly it is possible that the smoke constituent is preformed in the tobacco, as, for instance, nicotine. So the starting amount is constant and the variation arises from pyrolytic degradation. In another case the smoke constituent is formed by pyrolysis, as, for instance, the phenols.

A further phenomenon is an apparent alteration of the yields of the component in the main stream smoke caused by a component's escaping into the side stream smoke. In this case the total yield is constant. For this kind of shifted proportions between different smoke streams the expression "dismutation" was proposed.

From this point of view, filter retention is an alteration not of the total yield but of the yield of the component in the main stream smoke. The expression "selectivity", following a proposal made in Pully (79), ought to be reserved for the phenomenon of a filter having a different retention value for a certain component rather than for the total smoke or, better, for the total particulate matter. It should be borne in mind that by selective removal of a component the residual smoke is also altered. For this reason the total particulate matter is of no suitable reference value. A better reference would be a tobacco constituent which is neither formed nor altered during the burning processes. These conditions are fulfilled by the potassium ion proposed by Hjern (81).

Another point of discussion was the distinction between several smoke streams, which are given in Table 4 following a proposition by Lipp (80).

Meanwhile, several papers on transportation or dismutation phenomena have appeared; in 1966 Waltz, Häusermann, and Hirsbrunner (82) studied the transport of several components through the cigarette paper during puff and interval. They found that diffusion is important for water, while alkaloids diffuse only to a small extent through the cigarette paper. Generally, diffusion is 3 to 10 times more intensive during puffs than during intervals.

In simultaneous studies, but in different ways, Seehofer (83) and colleagues and our own group (84) estimated a water balance of burning cigarettes by analysis of the total smoke and elemental analysis of the cigarette tobacco.

About 63% of the hydrogen in tobacco is burnt during the smoking process. More than 95% of the water consisting of tobacco moisture and combustion water were detected in the side stream due to a very strong convection above the glowing zone and diffusion through the cigarette paper. This fact could be explained by the temperature profile in the axis of the burning cigarette which shows that the combustion zone and the zone of distillation are clearly separated from each other.

Papers by Seehofer (85) and his colleagues and our own group (86,

TABLE 4
Definition of various smoke streams (Lipp)

Place		Time	
		Puff	Interval
of deposition	Tobacco (butt)	Deposition on tobacco T	
	Filter	Adsorption on filter F	
of escape	Mouth piece	Main stream M	Smoulder stream S _m
	Paper	Diffusion stream D _p	Diffusion stream D _i
	Glowing cone	Glowing stream G _p	Glowing stream G _i

$$\text{Side stream } S = G_p + G_i + D_p + D_i + S_m$$

* Centre de Coopération pour les Recherches Scientifiques Relatives au Tabac.

TABLE 5

Selective filter retention (expressions)

Expression	Formula	Authors
Selectivity	$\Delta R = R_i - R_{TPM}$	Hoffmann, Wynder (103) Spears (93)
Relative retention difference	$\frac{\Delta R}{R_{TPM}} = \frac{R_i}{R_{TPM}} - 1$	Seehofer (104) Lipp (80)
Selectivity coefficient	$(\Delta\mu)_i = \mu_i - \mu_{TPM}$ from $K_i = K_{i0} \cdot e^{-\mu_i \cdot L}$	Fordyce, Hughes, Ivins (105)
Selectivity factor	$s_i = \frac{(g_i/g_{TPM}) \text{ filter}}{(g_i/g_{TPM}) \text{ smoke}}$	Davis, George (106)

TPM = total particulate matter, R = retention, i = substance i, g = weight

The influence of the tobacco type on the smoke composition was studied by Lipp (89). De Souza and Scherbak (90) found that glycerol fails to effect any major change in the production of benzo(a)-pyrene and in the total particulate matter of cigarette smoke. Sugawara, Ishizu, and Kobashi (91) found that smoke from cigarettes cased with sugars showed some increase in reducing substances, furfurals, nicotine, and tar, accompanied by a decrease in water and volatile acids. In 1965 Binopoulos, Kavazis, and Sficas (92) found a positive correlation between the resin content of the leaf and smoke condensate as well as between the nicotine content of smoke and leaf.

Much work has been done on the selective retention of filters. At the beginning of the period under review, two papers on the selective filtration of volatile phenols by cellulose acetate filters, by Spears (93) and Hoffmann and Wynder (94), appeared in 1963. In 1964 Waltz, Häusermann, and Moser (95) stated a selectivity of cellulose acetate filters for pyridine, which was confirmed by Kuhn (96) in a study presented during the congress. In 1965 Lipp (97) investigated the selective retention of nicotine in connection with the pH-value of the aqueous smoke extract and found a disrupted increase of about 50 to 100% in retention above pH 6. Later on, in 1965, Cuzin, Testa, and Testa (98) studied the selectivity of cellulose acetate filters on phenols, polyphenols, Ehrlich-positive substances, and indole. All pyrrol compounds among them are selectively absorbed like phenols. Fordyce and Horsewell (99) investigated the relation between selective filtration of nicotine relative to total particulate matter by conventional cellulose acetate filters and pH of the smoke. Differing degrees of selective filtration of nicotine arose from changes in the distribution between vapour and particulate phase and the influence of pH in determining this distribution and equilibration velocity. Le Roux (100) published a study on the mechanism of phenol filtration by cellulose acetate materials and plasticizers. Selectivity is brought about by hydrogen bonding additionally to adsorption. Urea and nicotine amide are capable of increasing the phenol retention. In a comprehensive study Waltz and Häusermann (101) found two factors influencing selectivity: "affinity", i. e. the chemical affinity between smoke constituents and filter materials, and "availability", i. e. the availability by the presence of a component primarily influenced by the vapour pressure in the gas phase of the substance. Williamson and Allman (102) studied the relative acetaldehyde retention of different cigarette filters by gas chromatography.

Table 5 gives a survey of the expressions proposed for selective filter retention which are simultaneously in use.

Organoleptic Investigations

Little work has been published on the field of organoleptic investigations, a point which was emphasized by the late Elia Isaacvitch Salzman (107) during the congress in Salisbury 1963. However, in 1964 Stedman and Stills (108) studied the influence of isovaleric and β -methylvaleric acid as constituents of Turkish tobacco on the organoleptic properties of these tobaccos. Pyriki and Moldenhauer (109), in 1963, could not recognize any influence of pectines on the quality of tobacco, in a study on this subject.

87, 88) on the influence of the moisture content of tobacco on smoke analysis contributed to the knowledge of transportation phenomena or dismutation and even on the problems of total yield. So the decreasing nicotine content in the main stream smoke with increasing moisture content of tobacco is due to transportation of the nicotine to the side stream. The total yield of phenols is influenced by tobacco moisture content causing a decrease of the total phenol yield with increasing moisture content, as found by both groups.

A tobacco treatment was studied by *Bach, Kuhn, and Kuffner* (110) in 1963. The reaction between nicotine and ethylene oxide yields the diion (Fig. 14). This compound was also isolated from treated tobacco.

FIGURE 14
N-(β -hydroxyethyl)-3-(N-methyl-2-pyrrolidiny)-pyridinium di ion

Smoke Analysis

As to analytical methods for tobacco and smoke some papers about smoke condensation should be mentioned first. The method reported by *Barkemeyer and Seehofer* (111) using liquids for the absorption of larger amounts of tobacco smoke in vibration or rotation traps working at normal or lower temperatures, and the cold trap by *Elmenhorst* (112), published in 1965.

There is a series of other studies with the aim to prepare tobacco smoke condensate under prevention of aging, e. g. a paper by our own group on a pressure smoking procedure (113), the capillary press by *Seehofer and Hanssen* (114) and the method by *Mathewson* (115) using a short glass capillary, which were published during the last three years.

The precipitation of the side stream smoke can be executed by devices developed by our own group (116) and was utilized as mentioned earlier for some balance and total yield studies (83, 84, 85, 88).

In 1965 *Keith and Tesh* (117) published a method for the measurement of the total smoke issuing from a burning cigarette, using a dead end cold trap with molecular sieve pellets as a source of suction.

As regards the analysis and group analysis of smoke constituents, there were many papers, which are listed in Table 6.

Some of these methods were necessary to enable the smoke chemists to perform the selectivity studies mentioned before. It should be stated that there is still a great lack of simple colorimetric methods for groups of substances which will render it possible to gain more insight into yield alterations and dismutation phenomena during the smoking process.

Tobacco Analysis

Table 7 gives a survey of the analytical methods published for tobacco during the last three years.

Physics of Smoke

Last but not least, the physical measurements and results must be dealt with. In 1965 *Norman and Keith* (151) made a study of the charged particles of unfiltered cigarette smoke. 44.6% of the particles are uncharged, 47.3% bear 1 charge, whilst only 6.9% of the particles were found to have two charges and 1.2% to bear more charges than two. *Norman and Keith* found almost equal numbers of positively and negatively charged aerosol particles in tobacco smoke.

The "5th Tobacco Colloquium 1963" made resolutions regarding the nomenclature of the air permeability of cigarette paper and related terms, which were reported by *Lipp* (152). The term "air permeability" is employed for all kinds of air passage through the paper, consisting of "porosity", due to the minute pores of the paper, and "perforation", due to larger pores formed by mechanical or electrostatical perforation. The part of puff volume which penetrates the paper of a cigarette is called "the degree of ventilation". The measurement of these phenomena was described by *Lipp* (153). In 1966 the same author (154) studied the influence of pressure on the measurement of porous and perforated papers. With porous papers the flow rate obeys the Hagen Poiseuille law, whereas in case of perforated papers the flow rate follows an equation which contains a nonlinear part obeying the Bunsen law. That means that measurement of air permeability of perforated papers has to be completed with a pressure drop similar to that in normal cigarettes.

TABLE 6

Further new methods for the analysis of tobacco smoke constituents*

Constituent	Authors	Methods used	Year
Hydroxyl compounds	Laurene, Cundiff, and Green (118)	gas liquid chromatography	1965
Carbonyl compounds	Laurene, Lyerly, and Young (119)	gas liquid chromatography	1964
	Weaving (120)	3-methylbenzothiazolone hydrazone hydrochloride	1965
Acids	Oakley, Weissbecker, and Resnik (121)	anion exchange gas liquid chromatography of esters	1965
	de Wet (122)	gas liquid chromatography oxidation	1963
	Perakis (123)	column chromatography paper chromatography, UV	1964
Benzo(a)pyrene	Pailer, Hübsch, and Kuhn (124)	thin layer chromatography, UV	1965
	Ayres and Thornton (125)	high temperature gas liquid chromatography isotope dilution technique	1965
Polycyclic hydrocarbons	Sawicki, Stanley, and Elbert (126)	thin layer chromatography fluorescence measurement, UV	1964
	Robb, Guvernator, Edmonds, and Baveley (127)	gas liquid chromatography	1965
	Neurath and Lorentzen (128)	4-aminoantipyrine	1963
Phenols	Smith and King (129)	p-nitrobenzene diazonium chloride, UV	1964
	Spears (130)	gas liquid chromatography	1963
	Crouse, Garner, and O'Neill (131)	gas liquid chromatography	1963
Pyrocatechol	Waltz, Häusermann, and Krull (132)	column chromatography, UV	1965
Scopoletin	Waltz, Häusermann, and Krull (133)	column chromatography, UV	1965
Pyridine	Waltz, Häusermann, and Moser (95)	Asmus et al., C1CN barbituric acid, UV	1964
Nicotinic acid, Nicotinamide	Wahl (134)	UV	1964
Heterocyclic N-compounds	Testa and Testa (135)	column chromatography, UV	1964
	Schultz and Spears (136)	gas liquid chromatography	1966
Water	Thome (137)	gas liquid chromatography	1965
pH-value	Grob and Artho (138)	potentiometry	1965

UV = UV- and visible measurements

* supplementary to the text

Concerning filling power and mechanical properties of tobacco and cigarettes there are papers of *Pietrucci* (155), who studied the filling capacities of French tobaccos in 1965, and in 1963 *Hübschen* (156) reported about an instrument for the measurement of the stamping volume of tobacco. *Seehofer*, *Lorenz*, and *Borowsky* (157) described an apparatus for the detection of irregularities in the tobacco filling of cigarettes.

Pullman and *Keith* (158) described a semi-automatic instrument for the measurement of the cigarette free burning rate, and *Artho* (159), in 1965, found the cigarette free burning rate to be largely determined by the kind of paper and type of tobacco used. In another paper *Hübschen* (160) investigated the sorption isotherm of cut tobacco and hysteresis.

Constituent	Authors	Methods used	Year
Nornicotine	Glock and Wright (139)	1,3-indanedione, UV	1963
	Mashkovtsev and Sirotenko (140)	isatin, tannin colorimetry	1963
Nicotine, Nornicotine, Anabasine	Winefordner and Moye (141)	thin layer chromatography phosphorimetry	1965
Volatile bases (non pyridine)	Neurath, Ehmke, and Müller (142)	acidimetry, UV	1964
Nitrate	Lipp and Dölberg (143) Neurath and Ehmke (71)	3,4-dimethylphenol, UV	1964
Nitrate, Nitrite	Dölberg (144)	Cd-reducer diazotation, UV	1965
Scopolin, Scopoletin	Dieterman, Lin et al. (145)	paper chromatography fluorescence measurement	1964
Chlorogenic acid, Rutin	Häusermann and Waltz (146)	aminoethyl diphenyl-borate, UV	1962
Chlorogenic acid	Oakley and Millham (147)	UV	1963
Menthol	Mitchell, Barbee, and Irby (148)	gas liquid chromatography	1963
Water	Waltz, Häusermann, and Moser (149)	near IR	1963
	Pullman, Hollenbeck, and Gibson (150)	microwave absorption	1965

UV = UV- and visible measurements

* supplementary to the text

CONCLUSION

I hope that this résumé of the recent developments represents an almost complete survey of tobacco and smoke chemistry today. It is difficult if not impossible to cover all important papers published on this subject and some of them have surely remained untreated. However, a great number of the publications mentioned have been contributed by members of CORESTA.

We may expect that during the time until the next congress many of the unsolved problems of this field of science will be solved and that valuable results for even further progress will be produced.

SUMMARY

During the last three and a half years remarkable progress has been made in tobacco and tobacco smoke research. The fact that tobacco and smoke constituents of interest generally occur in extremely low concentrations necessarily led to the development of sophisticated analytical methods which were found to be of general interest in microanalysis. The composition of the gaseous phase of tobacco smoke is by now well known owing to studies using a combination of high resolution gas chromatography and mass spectrometry. A great many compounds were identified for the first time in tobacco or tobacco smoke by means of analytical procedures newly developed or adapted from other research fields. Terms concerning the distribution of the total smoke to the different smoke streams have been defined, and the possibilities of selective retention of smoke components have been examined. The distribution of water consisting of tobacco moisture and of combustion water among the different smoke streams and other transportation phenomena in the burning process of a cigarette have been studied. Particle size distribution, the determination of the air permeability of cigarette paper, and the mechanical properties of tobacco have been investigated by means of physical measuring procedures.

Die Forschung über Tabak und Tabakrauch hat in den letzten 3½ Jahren ungewöhnliche Fortschritte gemacht. Die außerordentlich geringen Konzentrationen der interessierenden Bestandteile von Tabak und Rauch haben zur Entwicklung verfeinerter Analysenmethoden gezwungen, die von allgemeinem Interesse in der Mikroanalytik sind. Die Gasphase des Rauches ist durch Kombination von Gaschromatographie hoher Trennleistung und Massenspektrometrie recht genau bekannt. Eine große Anzahl von Verbindungen wurden im Tabak und Tabakrauch erstmalig gefunden, für viele Inhaltsstoffe wurden Analysenmethoden neu entwickelt bzw. aus anderen Gebieten adaptiert. Begriffe über die Verteilung des gesamten Rauches auf verschiedene Ströme wurden definiert und die Möglichkeiten einer selektiven Absorption von Rauchbestandteilen näher untersucht. Die Verteilung des Verbrennungs- und Feuchtwassers des Tabaks auf verschiedene Rauchströme und andere Transportphänomene wurden registriert. Physikalische Meßmethoden befaßten sich mit der Partikelgrößenverteilung und den Problemen, die bei der Messung der Luftdurchlässigkeit des Cigarettenpapiers auftreten, sowie mit den mechanischen Eigenschaften des Tabaks selbst.

RÉSUMÉ

Au cours des trois dernières années et demie la recherche sur le tabac et sur sa fumée a fait des progrès remarquables. Le fait que les constituants intéressants du tabac et de sa fumée se présentent à des concentrations extrêmement basses conduisait nécessairement au développement de méthodes analytiques raffinées offrant de l'intérêt général à la microanalyse. On sait maintenant assez bien la composition de la phase gazeuse de la fumée grâce à des travaux utilisant une combinaison entre la chromatographie gazeuse à haute résolution et la spectrométrie de masse. Bon nombre de composés ont été identifiés dans le tabac ou dans la fumée pour la première fois à l'aide de procédés analytiques nouvellement développés ou acquis d'autres champs de recherche. Les termes concernant la répartition de la fumée totale entre les divers courants de fumée ont été définis, et les possibilités de la rétention sélective d'un composant ont été étudiées. La répartition de l'eau fournie par l'humidité du tabac ou formée pendant la combustion entre les divers courants de fumée et d'autres phénomènes de transport se présentant pendant le processus de combustion de la cigarette ont été examinés. La répartition par dimensions des particules, la détermination de la perméabilité à l'air du papier à cigarette et les propriétés mécaniques du tabac ont été étudiées moyennant des procédés de mesure physiques.

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