GC-MS analysis of the "Semi-Volatiles" of cigarette smoke

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DOI: https://doi.org/10.1093/chromsci/8.4.218

GC-MS Analysis of the "Semi-Volatiles" of Cigarette Smoke*

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There is strong evidence that the approximately 1,300 substances identified in cigarette smoke represent less than half of the actual number of components. Whereas further identifications are predominantly accomplished after separating whole smoke into relatively small fractions of homologues, there is still great interest for direct analysis of the complex mixture.

Separations without preliminary fractionation have been reported for the gas phase (2,3) and for the vapor phase (4). This paper deals with the more volatile part (b.p. ca. 180-350°C) of the particulate phase of smoke for which the term of "semi-volatiles" (SV) has been applied (5). The SV roughly comprise one-fourth of the total number of smoke components.

The direct analysis of the SV has long been troubled by two problems. First it is difficult to prepare a representative sample of SV out of the total particulate matter of the smoke. The second problem lies in the simultaneous presence of important acidic (e.g. phenols) as well as basic (e.g. alkaloids) constituents, each group strongly affecting the resolution of the other.

The first difficulty is overcome by splitless injection (6,7) of a dilute solution of total particulate phase

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**Abstract of a Paper Published in German (1).*

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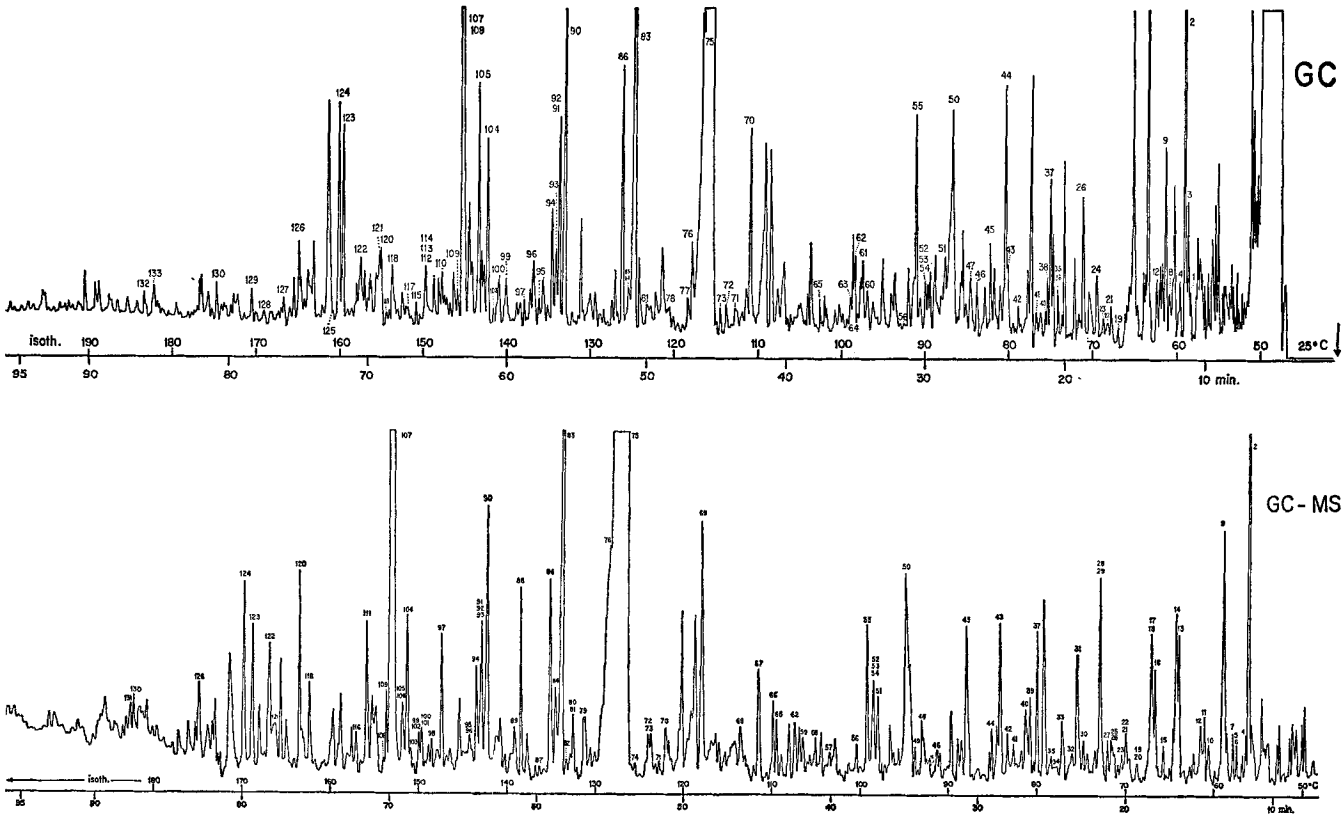

Figure 1. 4.0 μl of smoke solution injected with solvent bypassing without splitting on 1 m inlet capillary. Glass capillary column, 55 m/.35 mm coated with Emulphor O. Detection: GC: FID, GC/MS: total ion monitor.

Identified Components

(GC): by gas chromatography

(MS): by mass spectrometry

1	2,6-dimethylpyridine	(GS)
2	limonene	(GC) (MS)
3	pyridine	(GC)
4	methylpyrazine	(GC) (MS)
5	C_3-alkylbenzene	(MS)
6	n-undecane	(GC) (MS)
7	acetoin ?	(MS)
8	anisole	(GC)
9	2,5-dimethylpyridine	(GC) (MS)
10	C_3-alkylbenzene	(MS)
11	C_4-alkylbenzene	(MS)
12	3-methylpyridine	(GC) (MS)
13	C_4-alkylbenzene	(MS)
14	quinone ?	(MS)
15	C_3-alkylbenzene	(MS)
16	C_3'-alkylbenzene	(MS)
17	C_4-alkylbenzene	(MS)
18	C_3-alkylbenzene	(MS)
19	2,4-dimethylpyridine	(GC) (MS)
20	C_4'-alkylbenzene	(MS)
21	2,3-dimethylpyridine	(GC) (MS)
22	n-dodecane	(GC) (MS)
23	indan	(GC) (MS)
24	2-vinylpyridine	(GC)
25	C_4-alkylbenzene	(MS)
26	furfural	(GC) (MS)
27	C_4'-alkylbenzene	(MS)
28	C_4'-alkylbenzene	(MS)
29	C_5-alkylbenzene	(MS)
30	methylanisole	(MS)
31	dimethylpyrazole	(MS)
32	methylanisole	(MS)
33	C_5-alkylbenzene	(MS)
34	C_4'-alkylbenzene	(MS)
35	indene	(GC) (MS)
36	durene	(GC)
37	pyrrole	(GC) (MS)
38	benzofuran	(GC)
39	vinylpyridine	(MS)
40	2-acetylfuran	(GC) (MS)
41	benzaldehyde	(GC) (MS)
42	n-tridecane	(GC) (MS)
43	tetralin	(GC) (MS)
44	1-tridecene	(GC) (MS)
45	5-methylfurfural	(GC) (MS)
46	benzonitrile	(GC) (MS)
47	dihydrobenzofuran	(GC)
48	methylindene	(MS)
49	methylindene	(MS)
50	propylene glycol	(GC) (MS)
51	acetylmethylfuran	(GC)
52	acetophenone	(GC) (MS)
53	n-tetradecane	(GC) (MS)
54	p-tolualdehyde	(GC) (MS)
55	furfuryl alcohol	(GC) (MS)
56	1-tetradecene	(GC) (MS)
57	$C_{15}H_{26}$	(MS)
58	$C_{16}H_{34}$	(MS)
59	$C_{15}H_{24}$	(MS)
60	menthol	(GC)
61	3-cyanopyridine	(GC)
62	naphthalene	(GC) (MS)
63	propiophenone	(GC)
64	aniline	(GC)
65	n-pentadecane	(GC) (MS)
66	$C_{15}H_{26}$	(MS)
67	$C_{15}H_{30}$	(MS)
68	methylacetophenone	(MS)
69	$C_{13}H_{22}O$	(MS)
70	2-methylnaphthalene	(GC) (MS)
71	benzyl alcohol	(GC) (MS)
72	1-methylnaphthalene	(GC) (MS)
73	n-hexadecane	(GC) (MS)
74	α-tolunitrile	(MS)
75	nicotine	(GC) (MS)
76	quinoline	(GC) (MS)
77	2,6-dimethylphenol	(GC) (MS)
78	1-methylindole	(GC) (MS)
79	dimethoxybenzene	(MS)
80	dimethylnaphthalene	(MS)
81	biphenyl	(GC) (MS)
82	dimethylnaphthalene	(MS)
83	phenol	(GC) (MS)
84	n-heptadecane	(GC) (MS)
85	1,6-dimethylnaphthalene	(GC) (MS)
86	o-cresol	(GC) (MS)
87	dimethylnaphthalene	(MS)
88	$C_{19}H_{38}$	(MS)
89	methylquinoline	(MS)
90	p-cresol	(GC) (MS)
91	m-cresol	(GC) (MS)
92	o-ethylphenol	(GC) (MS)
93	2,5-dimethylphenol	(GC) (MS)
94	2,4-dimethylphenol	(GC) (MS)
95	n-octadecane	(GC) (MS)
96	acenaphthene	(GC) (MS)
97	1,2-dimethylindole	(GC) (MS)
98	1-octadecene	(MS)
99	acenaphthylene	(GC) (MS)
100	3,5-dimethylphenol	(GC) (MS)
101	trimethylphenol	(MS)
102	$C_{20}H_{40}$	(MS)
103	myosmine	(GC) (MS)
104	3-ethylphenol	(GC) (MS)
105	4-ethylphenol	(GC) (MS)
106	trimethylphenol	(MS)
107	neophytadiene	(GC) (MS)
108	3,4-dimethylphenol	(GC) (MS)
109	n-nonadecane	(GC) (MS)
110	2,3,5-trimethylphenol	(GC)
111	$C_{20}H_{38}$	(MS)
112	pyrocatechol	(GC)
113	eugenol	(GC)
114	carbazole	(GC)
115	7-methylindole	(GC)
116	trimethylphenol	(MS)
117	fluorene	(GC)
118	nicotyrine	(GC) (MS)
119	o-methoxyphenol	(GC)
120	n-eicosane	(GC) (MS)
121	glycerol	(GC) (MS)
122	isoeugenol	(GC) (MS)
123	vinylphenol	(GC) (MS)
124	indole	(GC) (MS)
125	coumarin	(GC)
126	3-methylindole	(GC)

127	2-methylindole	(GC)	
128	5-methylindole	(GC)	
129	trans-stilbene	(GC)	
130	n-docosane	(GC)	(MS)
131	3-ethylindole		(MS)
132	anthracene	(GS)	
133	phenanthrene	(GC)	

prepared by extraction of the loaded glass fiber filter with benzene/methanol (3+2). To produce the lower chromatogram in Figure 1, 4.0 μl of smoke solution were injected on the capillary column, using the solvent bypassing technique (7) without stream splitting. Under these conditions the SV were vaporized relatively slowly on a glass tube at 150°C into a 1 m long inlet capillary held at room temperature. After removing and cleaning the vaporizer tube retaining the less volatile substances, the inlet capillary was connected to the capillary column and analysis was started. At the given vaporizer temperature the substances eluted before m- and p-cresol were vaporized completely as proven by the fact that further heating of the vaporizer did not affect the peak heights for these substances whereas subsequent peaks became larger.

Simultaneous separation of acids and bases cannot be performed ideally since the adsorption of acidic substances on the column is intensified after the passage of a basic sample component, and vice versa. The column used was, therefore, pretreated to reduce adsorption of solutes to a minimum. The corresponding, purely inorganic modification of the glass surface is laborious and is still under study.

All separations were run on a full glass gas chromatograph from Carlo Erba, Milano, Model GI, as described earlier (6).

The upper chromatogram in Figure 1 was produced after connecting the column to the jet type molecular separator (8) of a mass spectrometer LKB 9000. This coupling procedure did not cause any significant loss of resolution. From the mass spectra it became evident that most of the approximately 350 peaks were still composed of two or more substances. We thus estimate that the actual number of SV constituents is at least around 1,000. We are continuing the work by using more efficient columns with the aim of extending as much as possible our knowledge of the composition of the SV.

Acknowledgment

This investigation has generously been sponsored by F. J. Burrus & Cie., Boncourt, Switzerland. ■

Manuscript received October 17, 1969

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