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Note

Quantitative determination of semivolatile compounds in cigarette smoke

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The term "semivolatiles" is used to describe the volatile fraction of the particulate phase of smoke[1], and this fraction includes compounds with boiling points up to 250°. Graham[2,3] used a fraction trapping and transfer device with two gas chromatographic (GC) columns to separate fractions of the semivolatiles. Six fractions of this portion of smoke were analyzed by Neurath *et al.*[4] using column chromatography followed by gas chromatography–mass spectrometry (GC–MS). Grob and Völlmin[5] analyzed the semivolatiles on a single chromatographic column without prior fractionation. The objective of this work was to develop a GC analysis that would serve as a fingerprint of this fraction of smoke and which could be used for the quantitative determination of certain semivolatile compounds.

EXPERIMENTAL

Sample preparation

An internal standard was needed to perform the comparative and quantitative analyses. Undecane (99% pure, Chemical Samples Co., Columbus, Ohio, U.S.A.) was used as the internal standard because it did not interfere with any peak of measurable size in the chromatogram. The internal standard solution was 14.8 μg of undecane/ml of a 1:1 mixture of acetone–methylene chloride.

One brand of domestic filter blend cigarettes was used to obtain the quantitative data. A cold trap[6] containing 4 ml of the internal standard solution was immersed in liquid nitrogen. The cigarettes were smoked under standard conditions (one 35-ml, 2-sec puff/min) to a 27-mm butt length on a Filtrona 20-port smoking machine connected directly to the trap. The whole smoke condensed as it came into contact with the cold glass. After forty cigarettes had been smoked into the trap, it was disconnected from the smoking machine and was warmed to room temperature. The whole smoke mixture was diluted to 5 ml with the internal standard solution.

Gas chromatographic conditions

An open tubular column was used for the separation of the semivolatiles. The 525-ft. × 0.012-in. I.D., glass capillary was coated with methyl silicone OV-101 liquid phase. The carrier gas, nitrogen, was regulated at a flow-rate of 1.85 ml/min

with a split ratio of 1:1. The column temperature was maintained at 30° for 12 min and was then programmed to 200° at 2°/min. A flame ionization detector was used to obtain the chromatogram shown in Fig. 1.

Mass spectrometric conditions

Mass spectra were recorded for the separated components of the complex semivolatile mixture with the Finnigan Model 1015 S/L gas chromatograph–mass spectrometer. The mass spectrometer serves as the detector for the gas chromatograph, and the signal for the total ion monitor is displayed on a strip chart recorder to obtain the chromatogram.

Quantitative data

Known amounts of the semivolatile compounds were added to portions of the internal standard solution. Three solutions, having approximately one-half the amount, equivalent amounts, and twice the amount of these semivolatile compounds present in forty cigarettes per 5 ml, were prepared. Then forty cigarettes were smoked into 4 ml of each of the three spiked solutions.

A peak height ratio between the peak height of each semivolatile compound and that of the internal standard was determined. A calibration curve was obtained from a plot of the peak height ratio *versus* the amount of the compound added. The point for the peak height in a control sample is on the ordinate, at 0 μg spiked. The amount of the compound in the control sample is the point where the calibration curve crosses the abscissa[7]. The amounts of sixteen of these semivolatile compounds identified are given in Table I.

TABLE I

QUANTITATIVE DETERMINATION OF SEMIVOLATILE COMPOUNDS IN A DOMESTIC FILTER BLEND CIGARETTE

Compound	*Amount (μg/cigarette)*
Benzene	23.0
Dihydropyran	0.6
2,5-Dimethylfuran	58.0
3-Heptyne	2.0
Ethylcyclopentene	0.3
Toluene	44.0
Pyrrole	4.0
m- and *p*-Xylenes	19.0
Styrene	18.0
o-Xylene	6.0
Cumene	0.8
Benzaldehyde	48.0
Benzonitrile	20.0
Limonene	64.0
Indene	2.0
p-Cresol	14.0

RESULTS AND DISCUSSION

The objective of this work was not to identify new compounds in cigarette smoke but to develop a rapid method to obtain an overall chromatographic picture of the semivolatile fraction of smoke. The analysis of the semivolatiles requires approximately 2 h and includes compounds with boiling points of 80° (benzene) to 246° (nicotine). An elaborate system of traps, extractions, valves, and chromatographic columns was avoided to give a simple analysis.

The compounds identified in the semivolatile fraction and the methods of identification are given in Fig. 1 and Table II. Certain of these compounds were quantitatively determined on a popular domestic filter blend cigarette (Table I). This GC method can be used to compare the amounts of these compounds in various cigarettes.

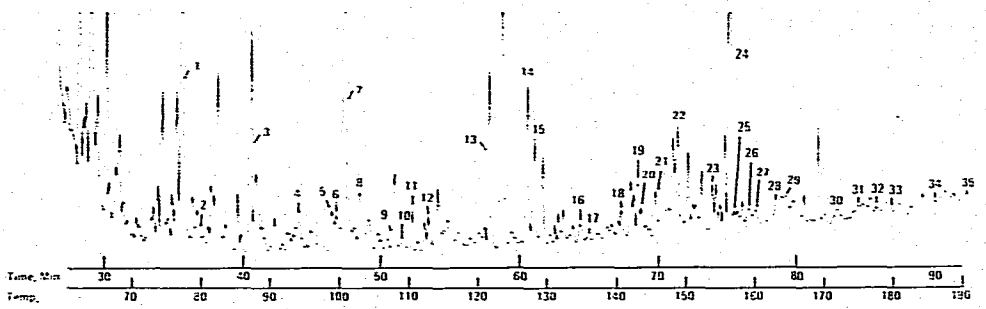

Fig. 1. Gas chromatogram of semivolatiles of a domestic blend filtered cigarette. See Table II for peak identification.

TABLE II

SEMIVOLATILE COMPOUNDS IDENTIFIED IN CHROMATOGRAM IN FIG. 1

No.	*Compound*	*Method of identification*	*No.*	*Compound*	*Method of identification*
1	Benzene	GC,MS	18	Benzaldehyde	GC,MS
2	Dihydropyran	GC	19	C_3-Benzene	MS
3	2,5-Dimethylfuran	GC,MS	20	Benzonitrile	GC,MS
4	Vinylcyclopentene	MS	21	C_3-Benzene	MS
5	3-Heptyne	GC,MS	22	C_3-Benzene	MS
6	Ethylcyclopentene	GC	23	Diethylbenzene	MS
7	Toluene	GC,MS	24	Limonene	GC,MS
8	Paraldehyde	GC	25	Indene	GC,MS
9	Pyrrole	GC,MS	26	Phenol	MS
10	Dimethylhexadiene	MS	27	C_4-Benzene	MS
11	2-Methylpyrazine	MS	28	Methoxyphenol	MS
12	Furfural	GC,MS	29	*p*-Cresol	GC,MS
13	*m*- and *p*-Xylenes	GC,MS	30	Methylindane	MS
14	Styrene	GC,MS	31	Methylindene	MS
15	*o*-Xylene	GC,MS	32	C_5-Benzene	MS
16	Cumene	GC,MS	33	Naphthalene	GC,MS
17	5-Methyl-2 furaldehyde	GC,MS	34	Ethylphenol	MS
			35	Trimethylphenol	MS

Most of the values given in the literature for the amounts of these compounds in cigarette smoke are for unfiltered cigarettes[3,8]. Both limonene and 2,5-dimethylfuran (Table I) were present in the domestic filter blend cigarettes in considerably larger quantities than reported previously. Smaller amounts of other compounds were found because they were selectively removed by cellulose acetate filters.

A highly precise method was sacrificed for one that could be performed routinely. The compounds that are determined quantitatively are representative of different classes of compounds containing various functional groups. Correlations can be made between the presence and amounts of these compounds and the presence and amounts of similar compounds known to be present in cigarette smoke.

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