

CIGAR BUTT AROMA. I. A PRELIMINARY STUDY OF CIGAR BUTT HEADSPACE VAPORS

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INTRODUCTION

In an attempt to identify the constituents responsible for the aroma of cigar butts we have begun a study of the volatile components of the headspace vapor from cigar butts. To our knowledge, no previous studies of the headspace vapors of cigar or cigarette butts have been reported. After collection and fractionation of the headspace vapors several of the major components were identified by infrared and mass spectrometry, and gas cochromatography.

EXPERIMENTAL

One thousand cigars were smoked under standard conditions (3). The cigars used in this study were prepared by the Cigar Manufacturers Association of America and were identical in all respects except for the filler tobaccos (2). Approximately equivalent amounts of the four filler tobaccos were used. The smoking conditions used were one 35 ml puff of two seconds duration every half minute until a butt length of 40 mm was obtained.

When the cigars had been smoked to the desired butt length, the butts were placed in a one liter flask and extinguished by cutting off the air supply. No attempt was made to segregate the butts on the basis of filler type. Each flask containing about 80 butts was subjected to a vacuum of 4 mm of Hg for two weeks. The vacuum system (Figure 1) allowed the butt headspace vapors to condense in a trap cooled by Dry Ice-acetone.

The condensate consisted of an aqueous layer and a very small yellow organic layer. Fractionation of the butt condensate commenced after one third of the butts had completed the vacuum treatment. The organic layer was extracted from the water with ether, and the ether solution was concentrated on a rotating vacuum evaporator at 10°C. Gas chromatographic analysis of the dis-

tillate showed no chromatographic peaks which were not attributable to the solvent.

The concentrated ether solution of butt condensate⁴ was fractionated on a Varian Aerograph Model 1520 Gas Chromatograph.³ The column was 10 ft. x 1/8 in. stainless steel packed with Chromosorb W (45-60 mesh) coated with FFAP (Free Fatty Acid Phase is a modified Carbowax 20M) liquid phase (18%). The column temperature was programmed on a matrix programmer from 50°C at 2°C/min for 25 min, 4°C/min for 10 min, 2°C/min until the column reached 190°C and then held isothermally at 190°C for 20 min. Carrier gas (helium) flow was adjusted for 30 ml/min at 55°C; injector and thermal conductivity detector temperatures were maintained at 250°C. Groups of peaks were collected as shown in Figure 2.

Peaks were partially purified by rechromatography on a 10 ft x 1/8 in stainless steel column packed with Chromosorb W (60-80 mesh) coated with SE-30 liquid phase (13.5%). The column temperature was programmed isothermally at 60°C for 10 min and 2°C/min thereafter. Carrier gas (helium) flow was adjusted for 30 ml/min at 55°C; injector and thermal conductivity detector temperatures were maintained at 250°C.

The eluates corresponding to the major peaks in the SE-30 chromatograms were collected in capillary tubes cooled by Dry Ice. Spectral data were obtained from the condensed eluates. Infrared spectra were obtained from a film of undiluted eluate contained in an ultramicro cell. After identification had been made from the infrared and mass spectral data authentic samples were cochromatographed with the original sample for final confirmation.

RESULTS AND DISCUSSION

It was necessary to resort solely to gas chromatography to separate the components of the "butt condensate" since the quantity of ether-soluble organic material from 1000 cigar butts was extremely small (crude estimate, 400 mg). It has been determined by gas chromatography of the aqueous fraction of the "butt condensate" that some compounds remain in the water even after extraction with ether. Also, several very volatile compounds, e.g., ammonia, methylamine, and acetaldehyde, may have been lost by the vacuum collection method which we have employed. Work is currently being conducted in both of these areas to insure a complete picture of the butt headspace vapor.

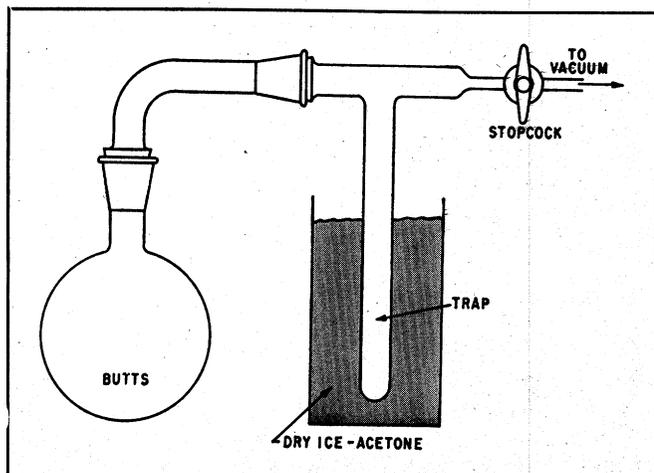


Figure 1—Vacuum system for collection of cigar butt headspace vapors.

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³Mention of a specific commercial product does not constitute an endorsement by the Department over similar items not mentioned.

⁴In this paper the term "butt condensate" refers to the condensed cigar butt headspace vapors.

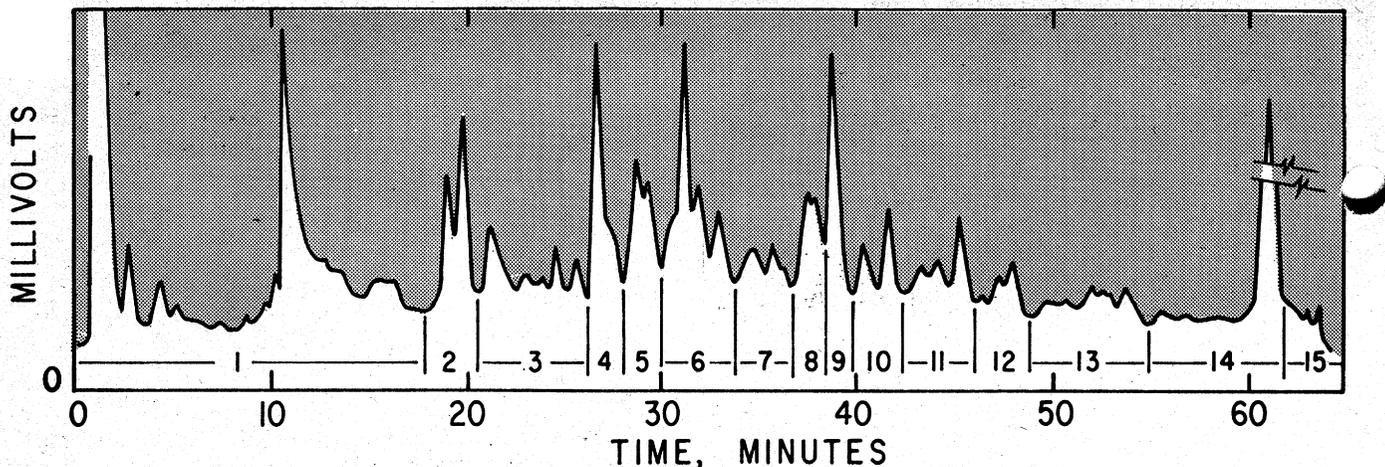


Figure 2.—Chromatogram of cigar butt headspace vapors on FFAP column.

A typical chromatogram of the ether solution of the "butt condensate" on the FFAP column is illustrated in Figure 2. Single peaks or groups of peaks were collected as indicated and rechromatographed on the SE-30 column. In almost every case this was necessary since what appeared to be one peak on the FFAP column was in actuality a mixture of several different compounds. Using this technique in conjunction with spectral examination of the eluates we have identified the following compounds in the indicated groups of peaks shown in Figure 2: group 2, pyridine and dipentene; group 4, 3-picoline; group 6, 3-ethylpyridine; group 8, 3-vinylpyridine, group 9, pyrrole; group 10, benzaldehyde; group 11, benzonitrile; and group 14, nicotine. With the exception of benzonitrile, all of these compounds are known constituents of tobacco smoke. Benzonitrile⁵ is a pyrolytic product of nicotine (1).

At this time it is not known whether any of these constituents contribute to the aroma of cigar butts. It

⁵During preparation of this manuscript benzonitrile was reported in cigar and cigarette smoke by E. Glock at the 22nd Tobacco Chemists Research Conference, Richmond, Va., October 17-19, 1968.

is possible that no single compound is the sole cause of the butt odor. A mixture of compounds which act in a concerted manner may be responsible. A synthetic mixture of the above compounds does not appear to simulate the odor of cigar butts.

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