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# Analysis of Volatile Pyrolytic Products of Tobacco Constituents: Stearic Acid Pyrolysis*

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## INTRODUCTION

Based on the development of thermally stable porous polymers (1), trapping systems have been reported for biologically important volatiles (10—12) and air pollutants (2). We have modified and refined such techniques for the routine analysis of volatile pyrolyzates. Volatile products may now be subjected to gas chromatography without resorting to vacuum manifolds, cryogenic techniques, or gas-sampling valves. Volatile organic compounds from pyrolysis reactions can be trapped, "fractionated", transferred to the gas chromatograph, and analyzed in less than two hours. One sampling of a pyrolyzate volatiles-adsorbent mixture may serve for multiple determinations. The application of this trapping technique to the analysis of volatile pyrolysis products in the pyrolysis of a mg quantity of stearic acid is described.

## MATERIALS AND METHODS

### *Adsorbents for Trapping*

Tenax GC** was obtained from Applied Science Laboratories, Inc., State College, Pennsylvania, USA. Carbosieve B was purchased from Supelco, Inc., Bellefonte, Pennsylvania, USA. Molecular Sieve 5A is available from numerous sources.

### *Pyrolytic Apparatus and Procedure*

The pyrolysis train consisted of a heated chamber, containing a pyrolysis tube, to which three traps were attached (Fig. 1). This apparatus allowed the insertion of the ceramic pyrolysis boat, with sample, into the preheated chamber at a constant rate. The rate of boat movement into the pyrolysis tube could be varied incrementally from 0.075 to 1.460 cm/min by means of a gear box, built into the Monodrum (Henry Troemner, Inc., Philadelphia, Pennsylvania). The system was continuously flushed with nitrogen-air carrier gas, before and during pyrolysis. The pyrolysis boat was connected to the Monodrum by a nichrome wire which passed through the pyrolysis tube and exited through a serum-bottle stopper in the inlet adaptor. The serum-bottle stopper allowed the wire to be drawn toward the drum while the system was maintained under positive pressure. Beyond the serum-bottle stopper, the wire was attached to a length of nylon string, wound up by the Monodrum. All glass joints in the pyrolysis train were made pressure tight by inserting Teflon sleeves. Each trap [a 16 cm pyrex tube with ball and socket joints (size 18/7)], contained from 1 to 3 g of adsorbent, and was plugged at both ends with silanized glass wool.

Pyrolyses were carried out at 860° C in an air-nitrogen (79 %: 21 %) atmosphere. Carrier-gas flow rate was maintained at 20 ml/min for the duration of the experiment. For this experiment, the pyrolysis boat was charged with 5.0 mg of stearic acid. The boat was then attached to the nichrome wire and the apparatus reassembled. The system was flushed with air-nitrogen for five minutes, and the boat was then pulled into the middle of the pyrolysis furnace at a rate of 8.3 cm/min. Fifteen minutes after pyrolysis was

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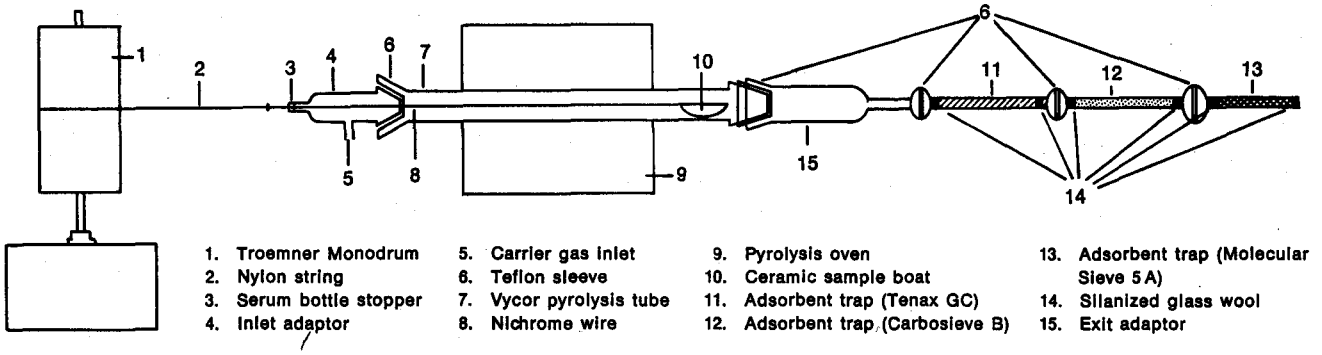
** Mention of commercial items does not imply their endorsement by the Department over similar products not mentioned.

**Figure 1. Pyrolysis train.**




1. Troemner Monodrum
2. Nylon string
3. Serum bottle stopper
4. Inlet adaptor
5. Carrier gas inlet
6. Teflon sleeve
7. Vycor pyrolysis tube
8. Nichrome wire
9. Pyrolysis oven
10. Ceramic sample boat
11. Adsorbent trap (Tenax GC)
12. Adsorbent trap (Carbosieve B)
13. Adsorbent trap (Molecular Sieve 5A)
14. Silanized glass wool
15. Exit adaptor

started, the traps were removed, stoppered, and stored at −20° C, until gas chromatographic (GC) analyses could be carried out. Non-volatile pyrolysis products were collected in the pyrolysis tube exit adaptor, with little or no transfer onto the Tenax GC trap.

*Gas Chromatography and Sampling Techniques*

A Varian Model 2800 gas chromatograph with flame ionization (FI) and thermal conductivity detectors was used. The GC columns were packed with the same adsorbent as used in the traps. Tenax GC-adsorbed samples were analyzed on a 3 m × 2 mm stainless steel column packed with Tenax GC (60/80 mesh) and conditioned at 370° C. For the analysis of the sample adsorbed on Carbosieve B, the column was 1.5 m × 2 mm stainless steel tubing packed with Carbosieve B (80/100 mesh). Gases adsorbed on Molecular Sieve 5A were chromatographed on a 2 m × 2 mm stainless steel column packed with 100/120 mesh Molecular Sieve 5A.

The sample-containing adsorbents (SCA) were removed from cold storage, transferred into small flasks and weighed. A portion of the SCA was transferred into the injector inserts (10 cm lengths of 6 mm outside diameter tubing) and the flask with remaining adsorbent was reweighed. The injector insert, plugged with silanized glass wool, was placed into the injection port of the GC, with column oven and injector at ambient temperature. Although the inserts were initially installed without much difficulty from the column oven side, it was later found to be more convenient to introduce the injector inserts by removing the septum holder. However, it was necessary to drill out the septum end of the injector sufficiently to accomodate the glass tube. After insertion, the GC fittings were reconnected and the injection port rapidly heated to volatilize the trapped compounds. The injection port temperature was raised to 350° C for Tenax GC and Carbosieve B and to 300° C for Molecular Sieve 5A. This heating required no more than 20 minutes. For all three analyses, the column oven was maintained at 30° C for the first 20 minutes and then temperature programmed. The Tenax column was programmed at 20°/min from 30° C to 130° C and then at 8°/min to 370° C. The Carbosieve B column was programmed at 20°/min from 30° C to 350° C, and the Molecular Sieve 5A column at 10°/min from 30° C to 300° C. Maximum temperatures were maintained for 20 minutes. FI detectors were used for all analyses. Helium carrier gas flow rates were maintained at 15 ml/min for all three columns. The FI detector was kept at 350° C. Quantitation was carried out with a Hewlett-Packard Model 3380 A recording integrator (Hewlett Packard Corp., Avondale, Pennsylvania). A DuPont Model 21-492 mass spectrometer equipped with a Varian Model 1400 gas chromatograph served to identify the substances and to verify the GC data. Chromatographic conditions were the same as described above.

## RESULTS AND DISCUSSION

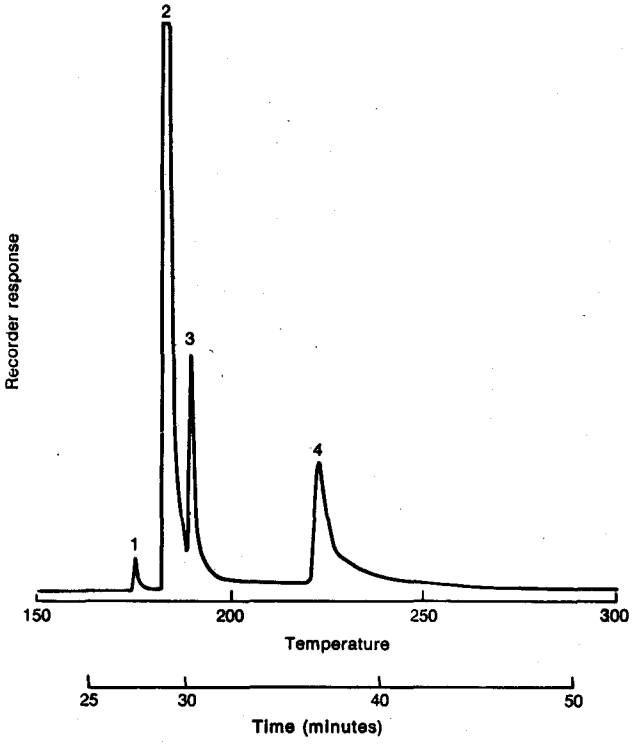
The described system can be used for the direct trapping and analysis of pyrolysis products of tobacco, tobacco constituents, or other organic materials. The pyrolysis products can be trapped on a series of adsorbents, arranged in decreasing order of polarity. The adsorbents employed in our system were Tenax GC, Carbosieve B and Molecular Sieve 5A. Porous polymers and other adsorbents are widely employed in gas chromatography. *Zlatkis* and coworkers (9) have used porous polymers in sampling volatiles from human breath and urine. Tenax GC, a porous polymer based on 2,6-diphenyl-p-phenylene oxide, is an excellent primary trapping agent, has efficient adsorptivity and desorptivity, and is stable to 370° C. However, for certain volatile pyrolyzates, consideration of selective retentions and thermal stability have indicated that other adsorbents are needed in addition to Tenax GC. At ambient temperatures, light hydrocarbon molecules (saturated and unsaturated), such a butanes and propylene, are not retained efficiently by Tenax GC. Therefore, a secondary adsorbent was added to trap the volatiles passing through the Tenax GC trap. Carbosieve B, a carbon molecular sieve, prepared by thermally cracking polyvinylidene chloride, has been thoroughly investigated as a material for gas chromatographic columns (7). This material had also been investigated as an adsorbent for trapping volatiles, but was rejected

**Table 1. Volatiles from the pyrolysis of stearic acid.**

| GC peak | Identification | Percent of combined sample[a] |
|---|---|---|
| 1 | acetylene | 0.41 |
| 2 | ethylene | 38.56 |
| 3 | ethane | 2.26 |
| 4 | propylene | 2.44 |
| 5 | 1,2-butadiene | 2.45 |
| 6 | 1,3-butadiene | 2.69 |
| 7 | 1-pentene | 2.47 |
| 8 | diethylether | 1.56 |
| 9 | 1-hexene | 1.19 |
| 10 | 1-heptene | 0.46 |
| 11 | iso- or 2-heptene | 0.37 |
| 12 | benzene | 6.81 |
| 13 | 1-octene | 0.45 |
| 14 | toluene | 1.34 |
| 15 | 1-nonene | 0.35 |
| 16 | xylene/decene | 0.50 |
| 17 | styrene/propylbenzene | 1.24 |
| 18 | undecene | 0.98 |
| 19 | methylstyrene | 0.42 |
| 20 | dodecene | 0.56 |
| 21 | ethylstyrene/dimethylstyrene | 0.26 |
| 22 | indene | 0.34 |
| 23 | naphthalene | 2.34 |

[a]Refers to material adsorbed both on Carbosieve B (peaks 1 — 4) and on Tenax GC (peaks 5 — 23).

**Figure 2. Chromatogram of stearic acid pyrolysis volatiles adsorbed on Carbosieve B.**




since the high temperatures necessary to desorb larger molecules would possibly pyrolyze some compounds (9). Carbosieve B was chosen for the second trap, since it was established that it efficiently adsorbs and desorbs

**Figure 3. Chromatogram of stearic acid pyrolysis volatiles adsorbed on Tenax GC.**

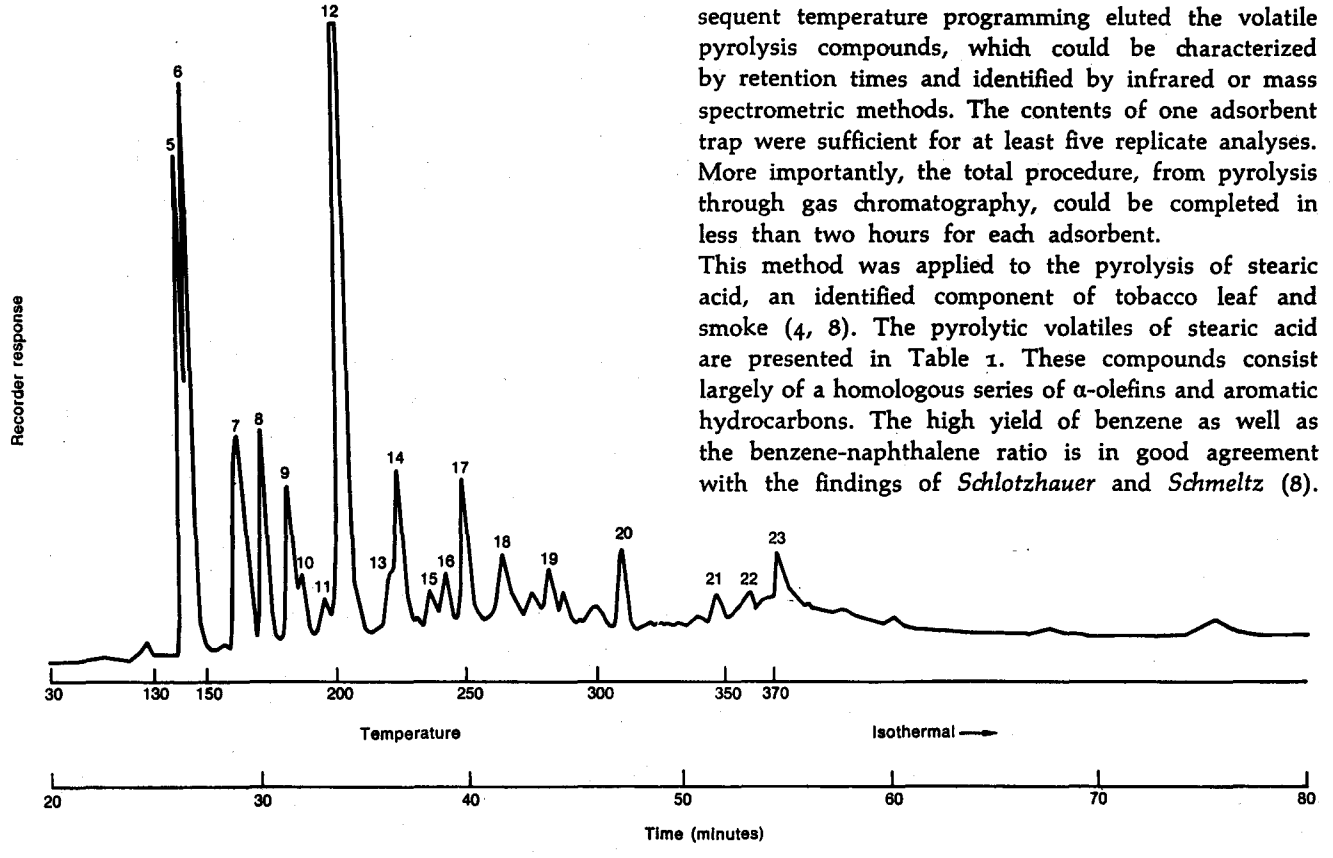
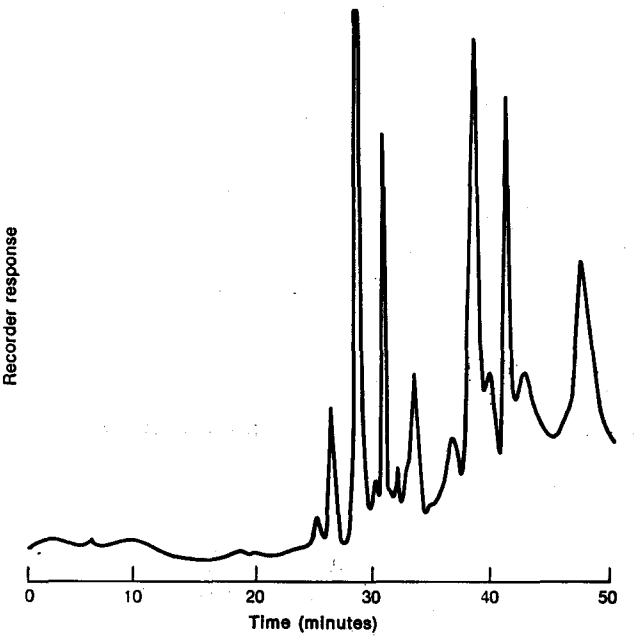



**Figure 4. Chromatogram of stearic acid pyrolysis volatiles adsorbed on Molecular Sieve 5A.**




many of the compounds contained in the effluent from the Tenax GC trap. A third trap may also be added to stop very light molecules that might pass through Carbosieve B. Molecular Sieve 5A is ideal for this purpose because of its strong affinity for small molecules, such as methane and carbon monoxide and also for its thermal stability.

Heating the volatile-containing adsorbents in the GC injection port resulted in the thermal desorption of the volatiles and deposition on the GC column. Subsequent temperature programming eluted the volatile pyrolysis compounds, which could be characterized by retention times and identified by infrared or mass spectrometric methods. The contents of one adsorbent trap were sufficient for at least five replicate analyses. More importantly, the total procedure, from pyrolysis through gas chromatography, could be completed in less than two hours for each adsorbent.

This method was applied to the pyrolysis of stearic acid, an identified component of tobacco leaf and smoke (4, 8). The pyrolytic volatiles of stearic acid are presented in Table 1. These compounds consist largely of a homologous series of α-olefins and aromatic hydrocarbons. The high yield of benzene as well as the benzene-naphthalene ratio is in good agreement with the findings of *Schlotzhauer* and *Schmeltz* (8).

They reported these two compounds to be the major components of the neutral fraction, obtained from the pyrolysis of stearic acid at 860° C.

Chromatograms for the volatiles trapped by the selected adsorbents are presented in Figures 2 to 4. Consecutive day-to-day sampling and comparison of chromatogram peak areas did not reveal any losses of volatiles from SCA during 5 days at −20° C. The chromatograms showed that different volatiles were trapped on each adsorbent. For the analyses, it was not necessary to cool the analytical column below room temperature nor was it necessary to install a precolumn, as required in earlier methods (3, 9). Pyrolysis volatiles adsorbed on the Molecular Sieve 5A constituted a small percentage of the total products, and were not of sufficiently high concentration to afford identification by mass spectrometry.

The use of the mixed air-nitrogen pyrolysis atmosphere was rationalized in the following manner. Cigarette smoke is an aerosol having a discontinuous phase (approximately 8% of the total weight) and a continuous phase composed of vapor constituents (19%), excess nitrogen (15%), and air (58%) (5). The air-nitrogen ratio is about 4 to 1. Consequently, it was decided to use an atmosphere consisting of 79% air and 21% nitrogen. This atmosphere would more closely approach actual smoking conditions than either of these gases alone.

Subsequent reports will deal with the application of this method to the analysis of volatile smoke and pyrolysis products of tobacco, tobacco constituents, additives, and agricultural chemicals. The importance of these volatile compounds becomes apparent when one considers that the particulate matter of tobacco smoke accounts for only about 8% of the total smoke (5).


## SUMMARY

A procedure has been developed to collect, transfer, and analyze volatile organic pyrolysis products of tobacco leaf compounds. The volatiles were collected in a series of three traps on adsorbents that also served as substrates for transfer and for introduction of the volatiles into a gas chromatograph. Analytical procedures are described for three gas chromatographic columns packed, respectively, with the three different adsorbents used in the traps. With this system, volatile pyrolyzates were collected and analyzed without the use of cryogenic traps, vacuum manifolds, or gas-sampling valves. The applicability of the procedures is demonstrated for the pyrolysis volatiles of stearic acid, a tobacco constituent.

## ZUSAMMENFASSUNG

Es wurde ein Verfahren entwickelt zum Auffangen, Übertragen und Analysieren flüchtiger organischer Pyrolyseprodukte von Verbindungen des Tabakblattes. Die flüchtigen Verbindungen wurden in drei in Reihe geschalteten Fallen auf Adsorbenzien gesammelt, die auch als Substrate zum Übertragen und Einführen der Verbindungen in einen Gaschromatographen dienten. Analytische Methoden werden für drei Gaschromatographie-Säulen beschrieben, die mit den drei verschiedenen, in den Fallen benutzten Adsorbenzien gefüllt sind. Mit diesem System wurden die flüchtigen Pyrolyseprodukte gesammelt und analysiert, ohne daß Gefrierfallen, Vakuumleitungen oder Gasprobenventile benutzt wurden. Die Anwendbarkeit des Verfahrens wird für die flüchtigen Pyrolyseprodukte am Beispiel der Stearinsäure, einem Tabakinhaltsstoff, dargestellt.

## RESUME

On a développé un procédé permettant de recueillir, de transférer et d'analyser les produits organiques volatils de la pyrolyse des composés de la feuille de tabac. Les substances volatiles ont été recueillies dans une série de trois pièges à adsorbant. Les adsorbants servent en même temps comme substrats au transfert et à l'injection des substances volatiles dans un chromatographe gazeux. La méthode analytique est décrite pour les trois colonnes, contenant respectivement les trois adsorbants des pièges. Par ce procédé les pyrolysats volatils sont recueillis et analysés sans avoir recours à des pièges cryogéniques, conduites à vide ou valves d'échantillonnage de gaz. La possibilité d'application de cette méthode a été démontrée pour les produits volatils de la pyrolyse de l'acide stéarique, qui est un constituant du tabac.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