

CHROMSYMP. 404

CHROMATOGRAPHIC ANALYSIS OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

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SUMMARY

Fused silica capillary columns with thick films of cross-linked coatings have been used to separate many of the organic compounds that are present in the volatile fraction of automobile exhaust and in ambient air. Techniques have been developed that allow reversible collection and pre-concentration of organic compounds in ambient air on polymeric sorbents with minimal artifacts. The exhaust samples, which are directly injected without pre-concentration on sorbents, contain many of the same organic compounds that are found in sorbent-collected samples of urban ambient air. Similar anthropogenic organic compounds are not, in general, detected (<0.02 ppbV) in air samples from remote, rural areas in Colorado.

INTRODUCTION

Organic compounds play a fundamental role in the photochemistry of the atmosphere. Many of these compounds can undergo reactions with OH radical and ozone to produce oxidized species and aerosols. In polluted urban areas, organic compounds primarily from incomplete combustion of fossil fuels are important in the formation of photochemical smog and associated aesthetic and health problems. Oxidant formation in densely populated regions is strongly affected by various organic compounds. In pristine rural locations, vegetative emission of particularly reactive organic compounds such as isoprene and the monoterpenes may be important in the chemistry of the clean troposphere.

Because the mixtures of organic compounds in the atmosphere are so complex and the concentrations of some of the more interesting species are relatively low, sensitive and selective methods are required for analysis. Several techniques have been developed for pre-concentration of volatile organic compounds from the atmosphere, including sorption on porous polymers^{1,2}, cryogenic sampling with stainless-steel³ or glass containers⁴, and Tedlar bag sampling⁵. Each technique possesses inherent problems including irreversible adsorption, artifact formation^{6,7}, sample

* ppbV = part per billion by volume; 1 billion = 10⁹.

contamination⁵ and limitations on the types of compounds that can be concentrated and recovered⁸. After pre-concentration, the most widely used method of analysis is gas chromatography (GC) coupled with mass spectrometry (MS) or with flame ionization detectors.

The objectives of this study were to develop simple and effective methods for determination of the identities and concentrations of volatile organic compounds in auto exhaust, urban air and rural air.

EXPERIMENTAL

Exhaust sampling

Samples for the analysis of organic compounds in automobile exhaust were collected in 1-ml and 5-ml gas-tight syringes fitted with shut-off valves (Precision Sampling Corp., Baton Rouge, LA, U.S.A.). The samples were collected from the tail pipes of automobiles with idling engines at normal operating temperature by flushing the syringe five times with the exhaust gases.

Ambient air sampling

Volatile organic compounds in the atmosphere were collected by a Tenax sampling technique^{1,2}. Air samples (1 to 6 l) were drawn through 17 cm × 4.5 mm I.D. borosilicate glass tubes, containing 150 mg of Tenax-TA using a DuPont Model P4000 pump, operating at a flow-rate of 100–150 ml/min. Tenax-TA is a special form of poly(2,6-diphenyl-*p*-phenylene oxide), prepared from purified precursors to minimize contamination. The sample was provided by Dr. A. Venema (Akzo Research, Arnhem, The Netherlands); Tenax-TA has since been offered commercially. After conditioning by heating under a flowing helium stream at 300°C for 24–48 h, blanks were much lower than from Tenax-GC treated similarly. No solvent extraction purification of Tenax-TA is necessary.

Gas chromatography

Spark ignition and diesel exhaust samples were analyzed by split injections from a gas-tight syringe into a cooled fused silica capillary column. The temperature program used was 2 min at –60°C then 8°C/min to 200°C.

Ambient air samples sorbed on Tenax-TA were analyzed by thermal desorption at 250°C into a cooled fused silica capillary column for 10 min. The temperature program used was –60°C to 0°C at 20°C/min then 0°C to 250°C at 8°C/min.

Gaseous exhaust and Tenax-sorbed ambient air samples were analyzed with a Hewlett-Packard Model 5880A gas chromatograph and a Hewlett-Packard Model 5982A gas chromatograph–mass spectrometer that has been modified so that a fused silica capillary column is inserted directly into the ion source.

The fused silica capillaries used in this study were a 30 × 0.32 mm I.D. DB-5 column (J&W Scientific, Rancho Cordova, CA, U.S.A.) with a film thickness of 1 μm and a 25 m × 0.31 mm I.D. ULTRA No. 2 column (Hewlett-Packard, Avondale, PA, U.S.A.) with a film thickness of 0.52 μm. The stationary phase for both columns is a cross-linked 5% phenyl–95% methyl silicone.

RESULTS AND DISCUSSION

Direct analysis of the organic constituents of automobile exhaust using thick-film cross-linked phase capillary columns offers many advantages over techniques previously developed^{9,10}. A column with a 1.0- μm film thickness exhibits greater retentiveness for the most volatile species and can resolve most of the organic compounds in the exhaust. A single column can be used for the analysis of the wide range (C_1 - C_{12}) of compounds present. The cross-linked phase is stable to injections of large amounts of water and showed little or no decrease in performance after 50 injections of auto exhaust samples. The sampling procedure is simple, and the overall separation and determination is rapid (28 min) with good precision (relative standard deviation < 5%).

One of the major sources of organic compounds in urban areas is exhaust from internal combustion engines. Examples of the direct analysis of the organic constituents of automobile exhaust samples are shown in Figs. 1 and 2. In Fig. 1, the fuel used in a single-cylinder 4-cycle test engine was pure isooctane. This single-component test fuel was used to make it easier to determine which exhaust products came from partial combustion, as contrasted with unburned fuel. Even with a single-component fuel, a large number of volatile organic compounds are detected in the exhaust of spark ignition gasoline engines. An example of the analysis of the exhaust of a 1981 Mazda 626 automobile using unleaded gasoline is shown in Fig. 2a. In addition to the compounds observed from combustion of a pure fuel, many additional compounds, primarily unburned constituents of gasoline, are detected in this sample. An example of the organic compounds from the exhaust of a 1975 Mercedes-Benz 240-D diesel engine is shown in Fig. 2b. Substantially lower concentrations of the more volatile organic compounds are found in the exhaust from this diesel engine, although higher amounts of particulate matter are produced by diesel engines. The column

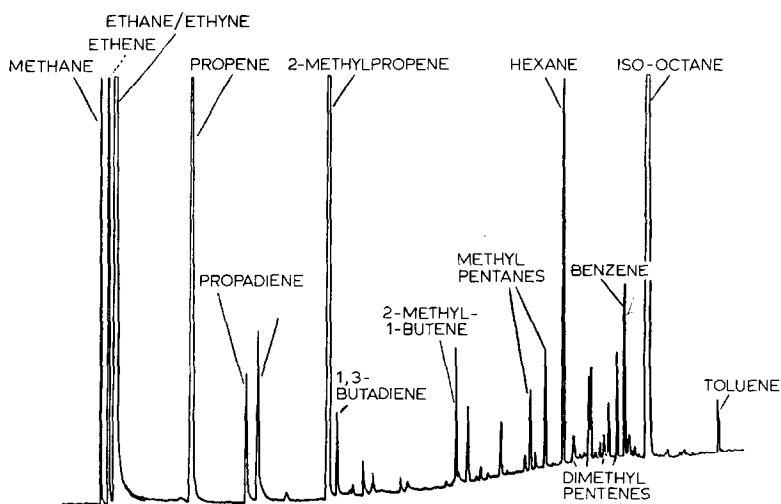


Fig. 1. Direct analysis of volatile organic compounds in exhaust from a test engine using pure isooctane. GC conditions: 1 cm^3 split injection (10:1); 2.5 min at -60° - 150°C at $8^\circ\text{C}/\text{min}$; 30 m \times 0.32 mm I.D. DB-5 column (1- μm film thickness); flame ionization detector (attenuation \times 1).

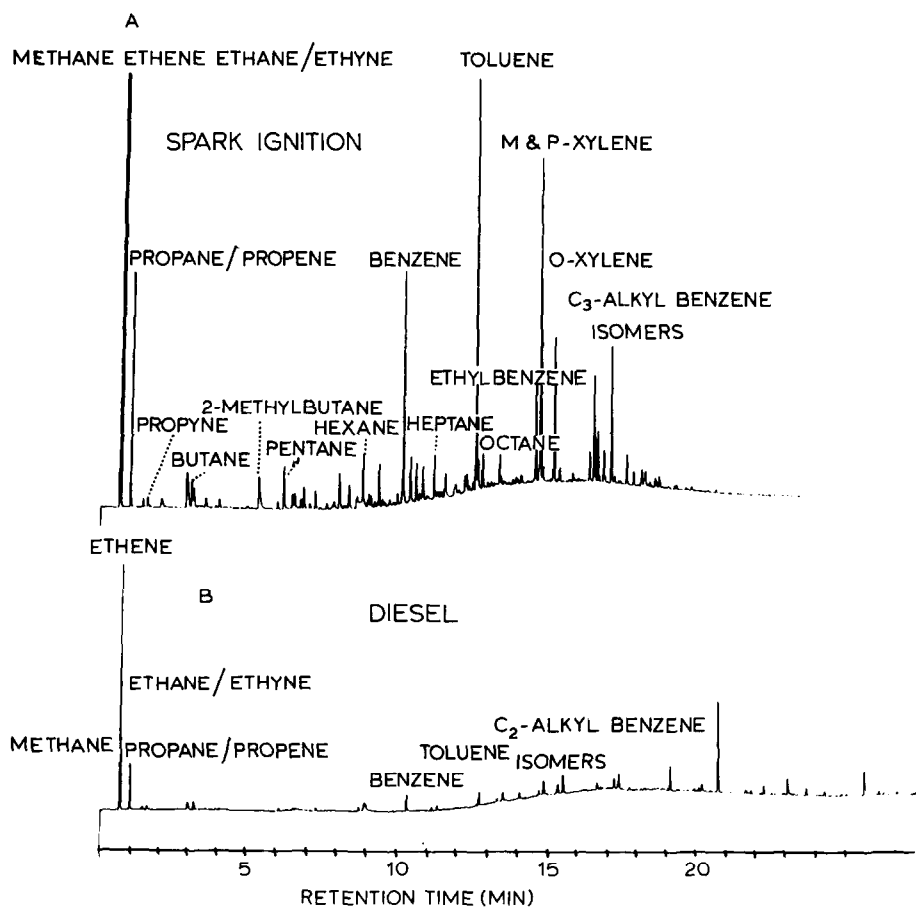


Fig. 2. Direct analysis of volatile organic compounds in exhaust from spark ignition (a) and diesel (b) engines. GC conditions: 1-cm³ split injection (15:1); 2 min at -60°-200°C at 8°C/min; 25 m × 0.31 mm I.D. ULTRA No. 2 column (0.52- μ m film thickness), flame ionization detector (attenuation × 2).

used in the analysis of the spark ignition and diesel exhaust samples has a film thickness of 0.52 μ m and the column used for the analysis of exhaust samples from the test engine using pure isooctane has a film thickness of 1.0 μ m. Better separation of the most volatile species is obtained by using the column with the thicker film.

Many of the organic compounds present in the exhaust of automobiles are found in the atmosphere of urban areas. An example of the volatile organic compounds present in the polluted air of Denver, CO, U.S.A. is shown in Fig. 3. The major compounds detected include normal alkanes from hexane to heneicosane, benzene, toluene, and C₂- to C₄-alkyl substituted benzene isomers. The concentration of benzene and toluene in 18 samples of Denver air collected in January and February, 1984, ranged from 2 to 8 ppbV and 1.5 to 25 ppbV, respectively. The winter-time concentrations of the normal alkanes ranged from 0.1 to 10 ppbV.

Other organic compounds detected in these samples include species from sources other than automobile exhaust. These include trichlorofluoromethane, di-

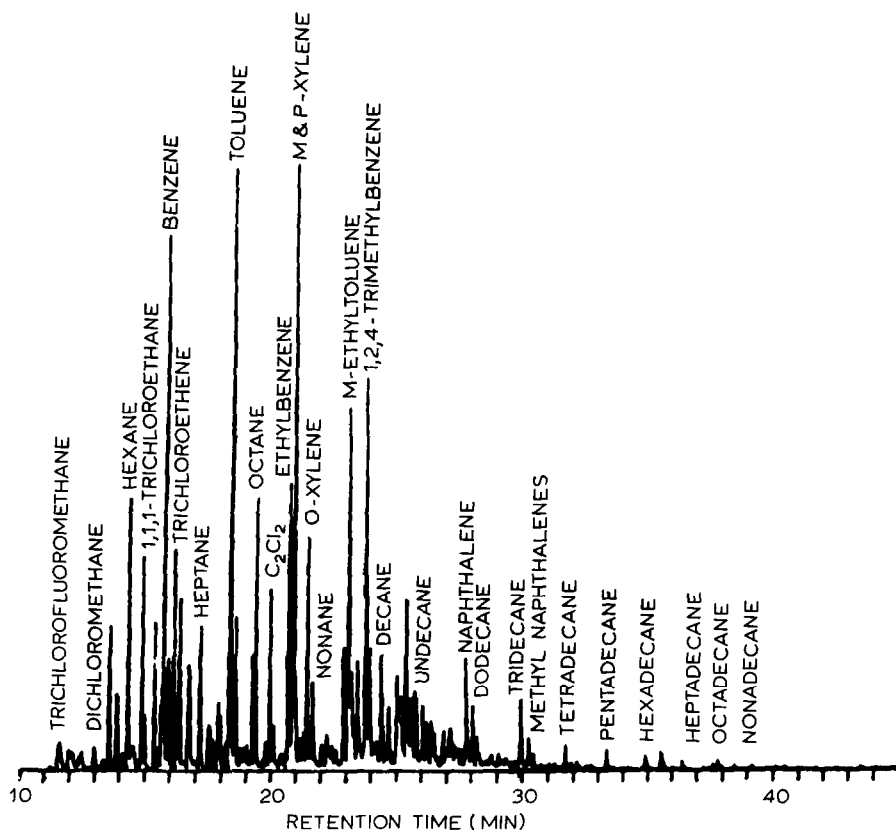


Fig. 3. Vapor phase organic compounds in ambient air of Denver, CO, U.S.A. A 5-l sample sorbed on Tenax-TA, desorbed at 250°C. GC conditions: 10 min at -60°C at 20°C/min then 0°-250°C at 8°C/min; 25 m × 0.31 mm I.D. ULTRA No. 2 column. MS conditions: electron impact (70 eV); 50-350 a.m.u. at 162.5 a.m.u./sec.

chloromethane, 1,1,1-trichloroethane, carbon tetrachloride and tetrachloroethene.

Air samples from a less populated urban area, usually with a less polluted atmosphere, *e.g.*, Boulder, CO, U.S.A., contain virtually the same organic compounds, but at concentrations as much as four times lower. Normal alkanes with molecular weights greater than that of hexadecane were not detected (<0.01 ppbV) in the vapor phase at this less polluted site, while they were detected in the air of Denver.

Air samples collected at rural sites in western Colorado generally contain organic compounds from both natural and anthropogenic sources. An example of the organic compounds detected in a wilderness area without local anthropogenic sources is shown in Fig. 4. It should be noted that the chromatogram was recorded at higher sensitivity settings than the chromatogram of urban air. The concentrations of aromatic and aliphatic hydrocarbons in samples with local anthropogenic sources are 10 to 100 times lower than those observed in polluted metropolitan areas. In samples collected in the Flat Tops Wilderness Area these compounds were not detected (<0.02 ppbV).

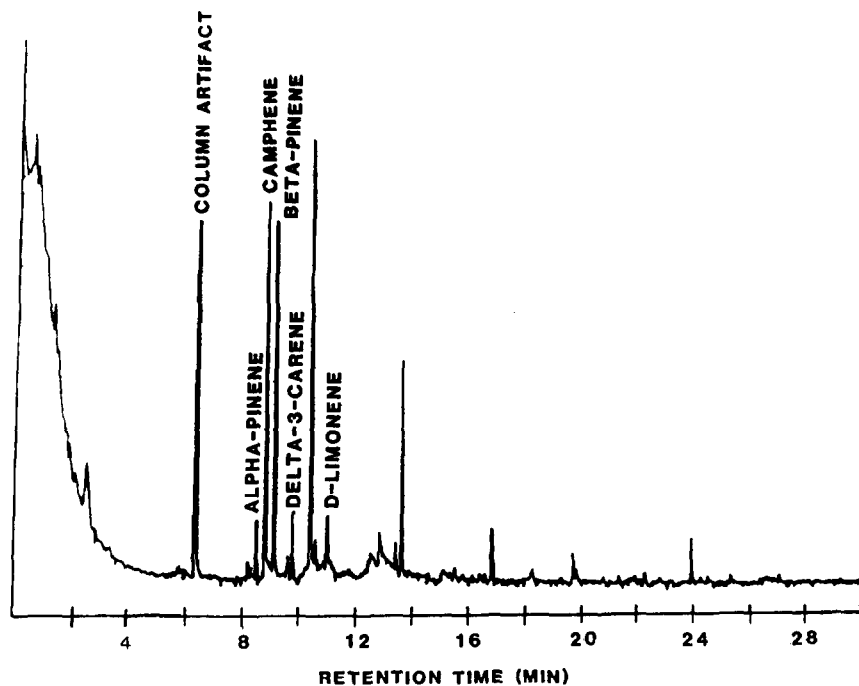


Fig. 4. Vapor phase organic compounds in ambient air of a wilderness area in Western Colorado. Six liter sample sorbed on Tenax-TA, desorbed at 250°C. GC conditions: 10 min at -50°C at $20^{\circ}\text{C}/\text{min}$ then 0°C - 250°C at $8^{\circ}\text{C}/\text{min}$, 25 m \times 0.31 mm I.D. ULTRA No. 2 column. MS conditions: electron impact (70 eV), 35-300 a.m.u. at 162.5 a.m.u./sec.

The most abundant volatile organic compounds in these rural samples were monoterpenes which generally were present at very low concentrations (0.02 to 0.2 ppbV). The major natural sources of these compounds are grasses, and coniferous and deciduous trees. Vegetation in the Flat Tops Wilderness Area is dominated by coniferous forests.

In air samples collected on Tenax-TA in both urban and rural areas, certain artifacts were invariably observed. These artifacts appear as peaks identified as benzaldehyde and acetophenone. These compounds are formed when the polymer is exposed to ozone^{6,7} and can potentially interfere with the analysis. While these artifacts cannot be totally eliminated, their formation can be minimized by using small sample sizes (0.5 to 2 l of air)¹¹.

ACKNOWLEDGEMENTS

The support of the Environmental Protection Agency under Project R 808312-01-0 and the National Science Foundation under Grant 81-08675 is gratefully acknowledged.

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