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## CONCENTRATION AND ANALYSIS OF TRACE IMPURITIES IN STYRENE MONOMER

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### SUMMARY

Trace levels of impurities in styrene monomer are collected at the exit end of a semi-preparative gas chromatographic column by passing the effluent gas into a tube containing the porous polymer Tenax. The major component, styrene, is not permitted to enter the adsorbent. The concentrated impurities are then thermally desorbed and analyzed by capillary gas chromatography and mass spectrometry. Of the more than 100 peaks present, 60 have been identified.

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### INTRODUCTION

The analysis of trace impurities at levels below 1 ppm does not lend itself well to conventional gas chromatographic (GC) methods. The use of highly sensitive specific detectors (electron capture, flame photometric and thermionic) have proved quite useful for compounds with a particular molecular composition. With other classes of compounds such as hydrocarbons, concentration techniques have been a necessary preliminary consideration. The recent development of Tenax GC by Zlatkis *et al.*, as a means of concentrating organic vapors in environmental<sup>1</sup> and biological samples<sup>2</sup> has made it possible to explore its use in the analysis of trace impurities in styrene monomer. Previous studies of commercial styrene<sup>3,4</sup> have shown the presence of 20 compounds.

The present investigation uses semi-preparative GC, Tenax trapping and high-resolution capillary GC-mass spectrometry (MS) to effect the concentration and analysis of 60 compounds which are present in styrene monomer. This technique involves the use of a 10- $\mu$ l styrene sample which is chromatographed on a semi-preparative column. The effluent of the column is attached to a small tube of Tenax during that period of the run when the styrene peak is not emerging. This allows collection of the impurities which elute both before and after the styrene peak. The direct analysis of trace impurities in 10  $\mu$ l of styrene is effected by thermal desorption of the compounds in the Tenax tube into a capillary GC-MS system.

This is a variation of heart-cutting<sup>5,6</sup> where instead of trapping a particular peak, the major component (styrene) is rejected and all of the impurities which elute before and after styrene are concentrated. Some of the compounds which stay in the styrene peak in a nonpolar column can be resolved by using a polar column.

## EXPERIMENTAL

### *Apparatus*

A Bendix Gas Chromatograph 2600 series with a flame ionization detector (FID) was used in these experiments. The column outlet system was modified to allow splitting of the effluent into a tube containing Tenax. The split was arranged so that 1% went to the FID.

### *Chromatographic columns*

Column A consisted of 8 m  $\times$  9.3 mm I.D. aluminum tubing packed with 20% w/w SE-30, (Supelco, Bellefonte, Pa., U.S.A.), on 30–60 mesh Chromsorb W; column B: 100 m  $\times$  0.5 mm I.D. nickel capillary tubing coated with Witconol LA 23, a polyoxyethylene lauryl ether (Witco, Houston, Texas, U.S.A.).

### *Chromatographic conditions*

Column A: 200° isothermal; nitrogen flow-rate, 37 ml/min. Column B: 60° isothermal for 15 min, then 100° isothermal for 30 min and finally programmed at 2°/min to 150°; nitrogen flow-rate, 5 ml/min.

### *Tenax adsorbent*

A tube 100  $\times$  10  $\times$  8 mm I.D. was filled with 4 ml of Tenax GC, 60–80 mesh, a porous polymer of 2,6-diphenyl-*p*-polyphenylene oxide. (Applied Science Labs., State College, Pa., U.S.A.). Glass wool was used at the ends of the tube. The Tenax was preconditioned at 300° for one hour in a stream of pure helium at 20 ml/min.

The GC–MS studies were performed on an LKB 9000 mass spectrometer, where the GC section was replaced with a Perkin-Elmer Model 900 gas chromatograph. A single stage jet separator was used. Ionization voltage was 70 eV, scan time for a mass range of 20–250 mass units was 4 sec. Scans were taken manually.

The mass spectra were interpreted by comparison with a library of spectra kept in our laboratory and with the aid of tabulated data<sup>7</sup>.

### *Procedure*

10  $\mu$ l commercial styrene (99.7%) was injected into column A with the Tenax tube connected at one arm of the split at the effluent end. This tube was removed just when the styrene peak was to appear (determined previously) and replaced after the styrene peak had almost returned to the baseline. The Tenax was then desorbed at 290° for 15 min at a helium flow-rate of 20 ml/min, as previously described<sup>8,9</sup>, and the components determined by capillary column GC–MS. Blanks were made on the total system without styrene. No peaks were present which interfered with the analysis.

## RESULTS AND DISCUSSION

The technique of concentrating the impurities by adsorption on a porous polymer is an effective method for the analysis of trace concentrations of organic compounds in styrene. More than 100 peaks were produced using this system and 60 listed in Table I were determined by capillary GC–MS. Indeed, by using larger samples,

TABLE I  
TRACE IMPURITIES PRESENT IN STYRENE MONOMER

Diethyl ether	Allylbenzene	Undecane	Pentadecane
Acetone	Methylstyrene	C <sub>5</sub> -Alkylbenzene	C <sub>9</sub> -Alkylbenzene
Hexane	Methylstyrene (isomer)	Tridecene	Diethyl phthalate
Methanol	C <sub>3</sub> -Alkylbenzene (isomer)	Tridecane	Hexadecene
Ethanol	Dichlorobenzene	C <sub>5</sub> -Alkylbenzene (isomer)	Hexadecane
Methylene chloride	Indane	C <sub>6</sub> -Alkylbenzene	Phenyl benzoate
Benzene	C <sub>4</sub> -Alkylbenzene	C <sub>7</sub> -Alkylbenzene	Dipropyl phthalate
Chloroform	C <sub>4</sub> -Alkylbenzene (isomer)	Biphenyl	1,3-Diphenylpropane
Toluene	Dimethylstyrene	Tetradecene	C <sub>10</sub> -Alkylbenzene
Ethylbenzene	Decahydronaphthalene	Tetradecane	Stilbene
<i>m,p</i> -Xylene	Limonene	Diphenylmethane	Heptadecane
Nonene	C <sub>4</sub> -Alkylbenzene (isomer)	Dimethyl phthalate	Diphenylbutene
<i>o</i> -Xylene	Acetophenone	C <sub>8</sub> -Alkylbenzene	Diphenylbutadiene
<i>n</i> -Propylbenzene	C <sub>4</sub> -Alkylbenzene (isomer)	Pentadecene	Diphenylbutadiene (isomer)
C <sub>3</sub> -Alkylbenzene	Methyl benzoate	1,1-Diphenylethylene	Dibutyl phthalate

0.1–1.0 ml, a considerably greater number of the trace constituents can be determined. The method employed is a reversal of heart-cutting and removal of the major constituent by venting. The adsorbed materials are easily stored for analysis at a convenient time. The use of both polar and nonpolar semi-preparative GC columns may help to move some of the compounds away from the major component.

The technique lends itself to the concentration and analysis of trace impurities in other commercial products. These include alcoholic beverages where water and ethanol are the major constituents and biological fluids which are primarily composed of water.

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