



## Project Summary

# Gas Chromatography/ Matrix Isolation-Infrared Spectrometry for Air Sample Analysis

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This report describes the application of gas chromatography/matrix isolation-infrared (GC/MI-IR) spectrometry to the analysis of several environmental air sample extracts. Samples that were analyzed include extracts from woodsmoke-impacted air, XAD-2 blanks, indoor air, and carpet samples. The emphasis of this report is on the use of GC/MI-IR to identify semivolatile organic compounds in these extracts. The complementarity of GC/MI-IR spectrometry and conventional electron-impact ionization gas chromatography/mass spectrometry (EI-GC/MS) is illustrated. The capability of GC/MI-IR to discriminate between isomeric compounds that are difficult to separate chromatographically and to distinguish by EI-GC/MS is demonstrated. Preliminary results regarding the potential of GC/MI-IR spectrometry for the quantitative analysis of polycyclic aromatic hydrocarbons in air sample extracts are presented. Problem areas and modifications of a commercial GC/MI-IR system are discussed.

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The capabilities of gas chromatography/matrix isolation-infrared (GC/MI-IR)

spectrometry for characterizing semivolatile organic compounds (SVOCs) in environmental air sample extracts were evaluated in this study. Since the development of GC/MI-IR spectrometry, several applications of the technique to the analysis of difficult samples have been reported in the literature. Many of these applications have been to environmental and health-related problems. Although several early reports of data obtained by GC/MI-IR dealt with the examination of the MI-IR spectra of environmentally important compounds, these studies were not direct applications of the technique to actual environmental samples. Thus, the capabilities, uses, and limits of GC/MI-IR for the analysis of real-world environmental samples must be determined.

In GC/MI-IR spectrometry, the effluent from the GC is trapped in an inert matrix as it is deposited on the surface of a rotating, gold-plated, cryogenic disk. The eluates remain frozen indefinitely on the disk and are analyzed by MI-IR spectrometry after the GC run is completed. Cryogenic trapping techniques, such as GC/MI-IR, offer several advantages over the more conventional, light-pipe-based GC/IR systems. The principal advantage is an increase in sensitivity. The increase in sensitivity is realized because the eluate is concentrated in a small cross-sectional area on the cryogenic disk, and most of each GC peak is interrogated by the IR beam during each scan. Also, because the eluate is frozen on the disk indefinitely, signal-averaging is allowed on any GC peak to increase the signal-to-noise ratio to the level necessary to obtain an identifiable



spectrum. Band broadening due to molecular rotation and intermolecular interactions is also minimized because the eluate is trapped in an inert matrix at a very low temperature. This results in sharper IR bands, which affords greater molecular specificity to aid in identifying components in complex mixtures and differentiating between isomers and other closely related compounds. In cryogenic-trapping GC/IR systems, the separation and detection of eluates are independent steps. Therefore, the chromatography and the spectrometry can be optimized without compromising one or the other.

In this report, we demonstrate the application of GC/MI-IR spectrometry to the analysis of extracts of woodsmoke-impacted air, indoor air, and carpet samples. Samples that were analyzed include the following:

- extracts of air samples collected on XAD-2 cartridges during a field study in a woodsmoke-impacted residential area
- extracts of XAD-2 blank cartridges that elicited an abnormally high bioassay response
- composite samples collected on quartz-fiber filter from woodsmoke- and mobile source-impacted areas
- a nitro-substituted polycyclic aromatic hydrocarbon (PAH) fraction of a pooled mobile source air sample and selected nitro-PAH standards
- selected polyurethane foam (PUF) and filter extracts from a pilot residential indoor air study
- extracts from air samples collected on XAD-2 cartridges in a complaint building
- extracts from selected carpet samples

The primary focus of the report is on the evaluation of the capabilities of GC/MI-IR for identifying specific SVOCs in complex environmental air sample extracts. The complementarity of GC/MI-IR and GC/mass spectrometry (MS) for the analysis of environmental samples is also illustrated. Most of the results described in this report pertain to the qualitative identification of unknowns in various sample extracts. We also present preliminary results regarding the potential of GC/MI-IR for quantitative analyses and discuss problems encountered with the GC/MI-IR system.

## Procedure

All GC/MI-IR data were collected on a Mattson Instruments (Madison, WI) Cryolect system. This system consists of a Mattson Instruments Sirius 100 Fourier transform IR spectrometer and Starlab data system, a Hewlett-Packard (HP) 5890A

capillary GC, and a Mattson Instruments matrix-isolation cryogenic module. In the Cryolect system, the effluent of the analytical GC column is split, with 20% directed to a flame ionization detector (FID); the remaining 80% is directed through an open-split cross and then through a heated, fused-silica transfer line to the cryogenic disk. The cryogenic disk is housed in an evacuated chamber and is maintained at 14 K during deposition and spectral analysis of the sample extract. The MI-IR spectra were obtained by coadding 128 scans at a nominal resolution of 4  $\text{cm}^{-1}$ .

The GC/MS results were obtained on an HP 5970B mass selective detector (MSD) interfaced to an HP 5980A capillary GC. Similar chromatographic conditions, including on-column injection, a (95%)-dimethyl-(5%)-diphenyl polysiloxane capillary column, and identical temperature programs, were used for both GC/MI-IR and GC/MS analyses.

## Results and Discussion

### *Extracts of XAD-2 Cartridges from a Field Study in a Woodsmoke-Impacted Residential Area*

Representative extracts of air samples collected onto XAD-2 cartridges during a field study designed to determine the impact of residential wood combustion on relatively simple airsheds were analyzed by GC/MI-IR and GC/MS. We analyzed extracts of air samples that were collected outdoors at night, outdoors during the day, indoors at residences with a wood-fired stove, and indoors at residences without a wood-fired stove. The chromatographic profiles of the different samples were qualitatively very similar, with each extract containing the same major components. Preliminary GC/MS analyses indicated that the major components of each extract were alkylbenzenes, including toluene, ethylbenzene, xylenes, ethyltoluenes, and trimethylbenzenes. Specific positional isomers could not be distinguished by GC/MS but were identified by GC/MI-IR. The MI-IR spectra of alkylbenzenes exhibit characteristic strong absorption bands between 1000 and 650  $\text{cm}^{-1}$ , which are due to the vibrational mode of the C-H out-of-plane deformation. The specific frequencies of these bands are determined by the position of the substituents on the ring and the number of adjacent hydrogen atoms remaining on the ring. Thus, the GC/MI-IR analysis of the XAD-2 extracts of the woodsmoke-impacted air enabled specific isomers, such as 3- and 4-ethyltoluene, to be identified even if they were not sepa-

rated chromatographically (see Figure 1). In addition to the alkylbenzenes, guaiacol (a potential woodsmoke tracer) was identified in an outdoor-nighttime residential air sample but was not detected in the indoor or daytime samples. Compounds identified in the indoor air samples, but not the outdoor samples, included *d*-limonene, 1,4-dichlorobenzene, normal aldehydes, and several alkanes.

### *Extracts of XAD-2 Blank Cartridges that Elicited an Abnormally High Bioassay Response*

Two concentrated extracts of XAD-2 blank cartridges that yielded abnormally high bioassay responses were analyzed by GC/MI-IR and GC/MS. Both extracts contained 2-ethyl-1-hexanol,  $\text{C}_4$ -benzenes, acetophenone, substituted acetophenones, an ethylstyrene, a silane, an unidentified aldehyde, naphthalene, and several esters, phthalates, and alkanes. One extract also contained two major components that were not detected in the other. One of these components was identified as 4-chlorophenylsulfone, and the other was tentatively identified as triphenylphosphine. No compounds were identified in the blank extracts that would be expected to contribute significantly to the mutagenicity of these extracts.

### *Quartz-Fiber Filter Composites from Woodsmoke- and Mobile Source-Impacted Areas*

Two nonpolar fractions of ambient filter composite extracts, a woodsmoke composite and a mobile source composite, were analyzed by GC/MI-IR and GC/MS. The chromatographic profiles of each extract were similar; both contained compounds associated with woodsmoke, such as 1-methyl-7-isopropylphenanthrene (retene) and the methyl ester of dehydroabietic acid, in addition to a series of alkanes and siloxanes and a large amount of background material. In spite of the large amount of background material present in the chromatogram, several PAH compounds, including fluoranthene, pyrene, 1-methylpyrene, and 5-methylchrysene, were identified in both extracts. By using GC/MI-IR, the presence of coeluting isomeric and closely related PAHs in the composite extracts was confirmed. For example, an unambiguous distinction between cyclopenta[*c,d*]pyrene and benz[*a*]anthracene was made, and the chrysene-triphenylene isomer pair was distinguished (see Figure 2).

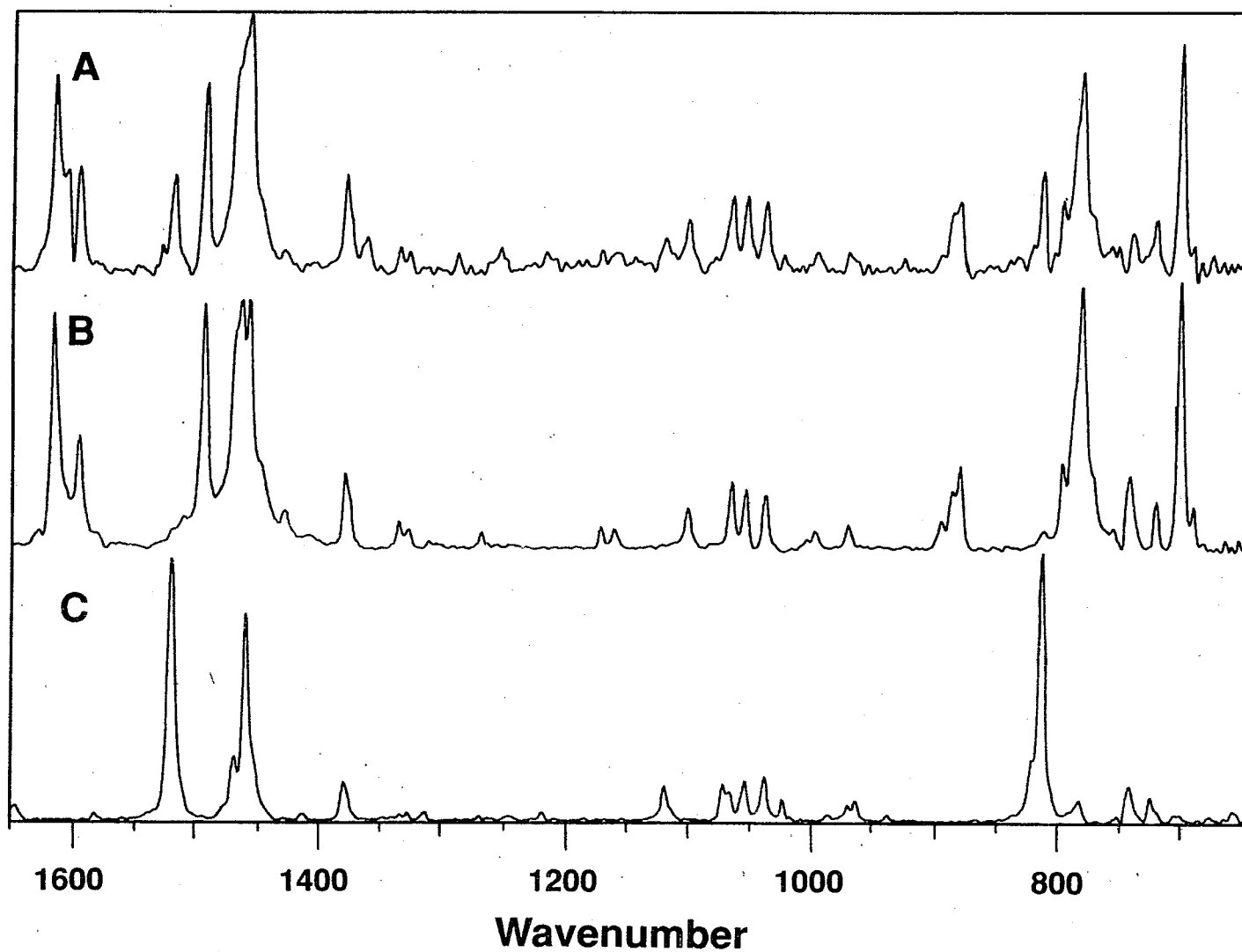
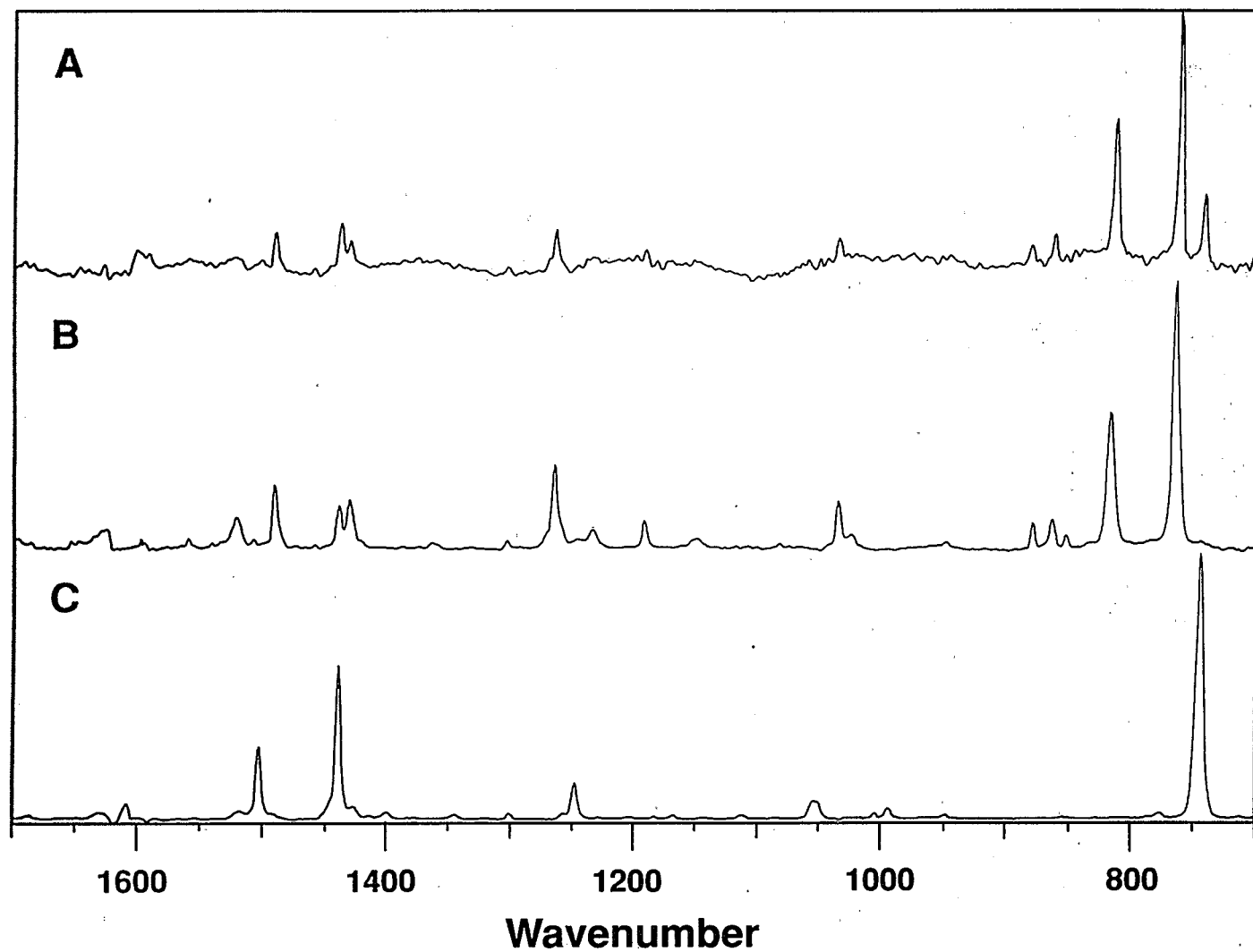


Figure 1. MI-IR spectra of (A) a component from an extract of an XAD-2 cartridge collected during a field study in a woodsmoke-impacted residential area, (B) 3-ethyltoluene reference standard, and (C) 4-ethyltoluene reference standard.



**Figure 2.** MI-IR spectra of (A) a component of a filter composite extract from woodsmoke- and mobile-source-impacted areas, (B) chrysene reference standard, and (C) triphenylene reference standard.

## **A Nitro-PAH Fraction and Selected Nitro-PAH Standards**

A nitro-PAH fraction of a pooled mobile source air sample extract was analyzed by GC/MI-IR. Reference MI-IR spectra of 1-nitropyrene, 2-nitrofluoranthene, 2-nitropyrene, and 6-nitrobenzo[a]pyrene were also acquired. Although high-quality MI-IR reference spectra of the standard compounds could be obtained, no target nitro-PAH were detected in the fractionated sample extract. The levels of nitro-PAHs in this fraction were estimated to be less than 100 pg/ $\mu$ L, which is below the detection limits of the GC/MI-IR system for these compounds. The reference spectra obtained on the GC/MI-IR system were comparable to MI-IR spectra of nitro-PAHs in the literature that were obtained under conventional slow-spray-on MI-IR conditions.

## **Selected PUF and Filter Extracts from a Pilot Residential Indoor Air Study**

Selected PUF and quartz-fiber filter extracts collected during a pilot residential indoor air study were analyzed by GC/MI-IR and GC/MS. The results from these analyses illustrated the difference in sensitivity and selectivity of GC/MI-IR and GC/MS for different chemical classes. For instance, the GC/MI-IR analysis showed the presence of a number of carbonyl-containing compounds, such as esters and carboxylic acids, whereas the scanning GC/MSD results were dominated by a series of long-chain, alkyl-substituted benzenes. The three-ring PAH isomers, phenanthrene and anthracene, were distinguished by GC/MI-IR in the presence of background material in the chromatogram of a PUF extract. Nicotine and tetraethylene glycol dimethylether were identified as the major components in an extract of SVOCs collected on a quartz-fiber filter in a smoker's home.

## **Extracts from XAD-2 Cartridges Collected in a Complaint Building**

The GC/MI-IR and GC/MS systems were used to analyze an extract of an XAD-2 cartridge collected from a room in an office complex during an episode of health-related complaints by employees. The extracts contained several *n*-alkanes, branched alkanes, and alkylated benzenes. Other major components of the extract that were identified included 2-butoxyethanol, benzaldehyde, 1,4-dichlorobenzene, an *n*-aldehyde,  $\alpha$ -terpineol, 4-phenylcyclohexene, and two 2,2,4-

trimethylpentane(1,3)diol isomers. The presence of 4-phenylcyclohexene, a by-product of the carpet manufacturing process and a suspected irritant associated with the characteristic odor of new carpet, prompted an investigation into the SVOCs and nonvolatile organic compounds associated with new carpet.

## **Extracts from Selected Carpet Samples**

Several carpet samples were Soxhlet-extracted in methylene chloride, concentrated, and then analyzed by GC/MI-IR and GC/MS. The GC/MI-IR analyses were used primarily to confirm tentative identifications made by GC/MS analyses. In addition, the unique features of MI-IR spectra, such as split carbonyl peaks and sharp O-H stretching bands, that are not found in condensed-phase or vapor-phase IR spectra aided in identifying components in the extracts.

In the analysis of these carpet samples, the GC/MI-IR results were used to confirm an error in a commercial mass spectral data base and to distinguish between SVOCs that have very similar mass spectra but significantly different MI-IR spectra, such as 6-aminohexanoic acid and  $\epsilon$ -caprolactam. The MI-IR spectrum of  $\epsilon$ -caprolactam exhibits a split in the carbonyl absorption band, which would normally indicate the presence of more than one carbonyl moiety (see Figure 3). However,  $\epsilon$ -caprolactam has only one carbonyl group. A search of the literature revealed that the MI-IR spectra of lactams, as well as many other compounds that contain a carbonyl group, can exhibit multiple carbonyl absorption bands. In the case of lactams, this multiplicity is attributed to the isolation of discrete conformers in the matrix. The MI-IR spectra of several phenols and diols identified in the carpet extracts exhibited sharp O-H stretching bands, which indicated the lack of intermolecular hydrogen bonding under the GC/MI-IR deposition conditions. The GC/MI-IR results were also used to identify background material, which was originally assigned to column bleed by interpretation of the GC/MS results, as an isocyanate.

## **Preliminary Investigation of the Quantitative Capabilities of GC/MI-IR**

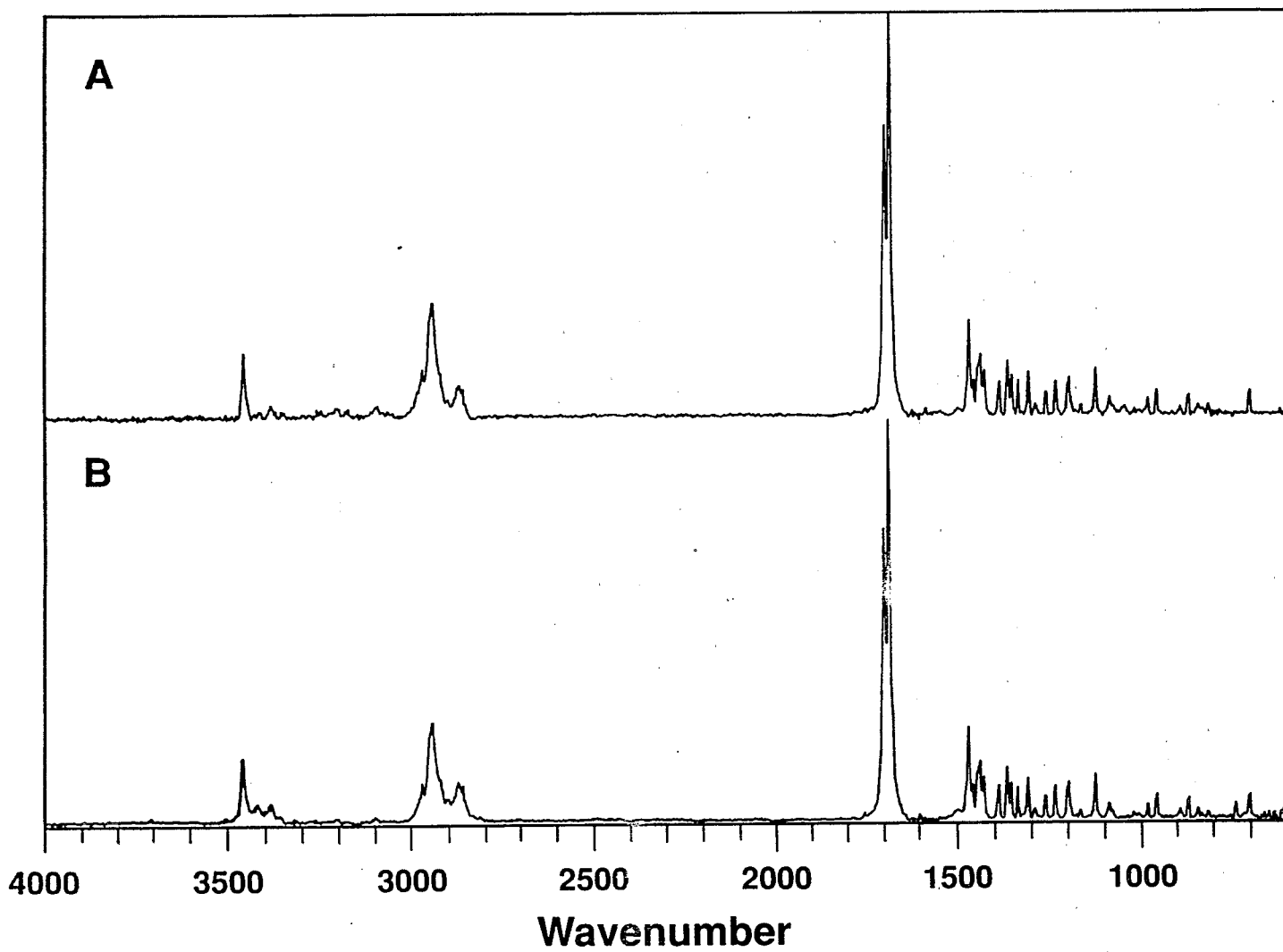
We have performed a preliminary investigation of the quantitative capabilities of GC/MI-IR spectrometry for the determination of target PAHs in environmental air sample extracts. Our initial goals were to determine the repeatability, the dynamic range, and the detection limits of the GC/MI-IR system for PAH compounds. To de-

termine the repeatability of the GC/MI-IR measurement, we analyzed replicate injections of a 10-ng/ $\mu$ L standard PAH mixture containing 10-ng/ $\mu$ L of 1-methylbenzo[a]anthracene as an internal standard. The MI-IR absorbance maximum of the analyte was normalized to the MI-IR absorbance maximum of the internal standard. Likewise, the FID peak area was normalized to the FID peak area of the internal standard. The average relative standard deviation of six replicate analyses was approximately 20% for the normalized MI-IR absorbance and on the order of 1% for the normalized FID peak areas. Because of the poor repeatability of the GC/MI-IR measurements, the dynamic range and the detection limits of the system for PAHs could not be determined. Fundamental experiments are currently underway to determine the sources of error in GC/MI-IR quantitative analyses.

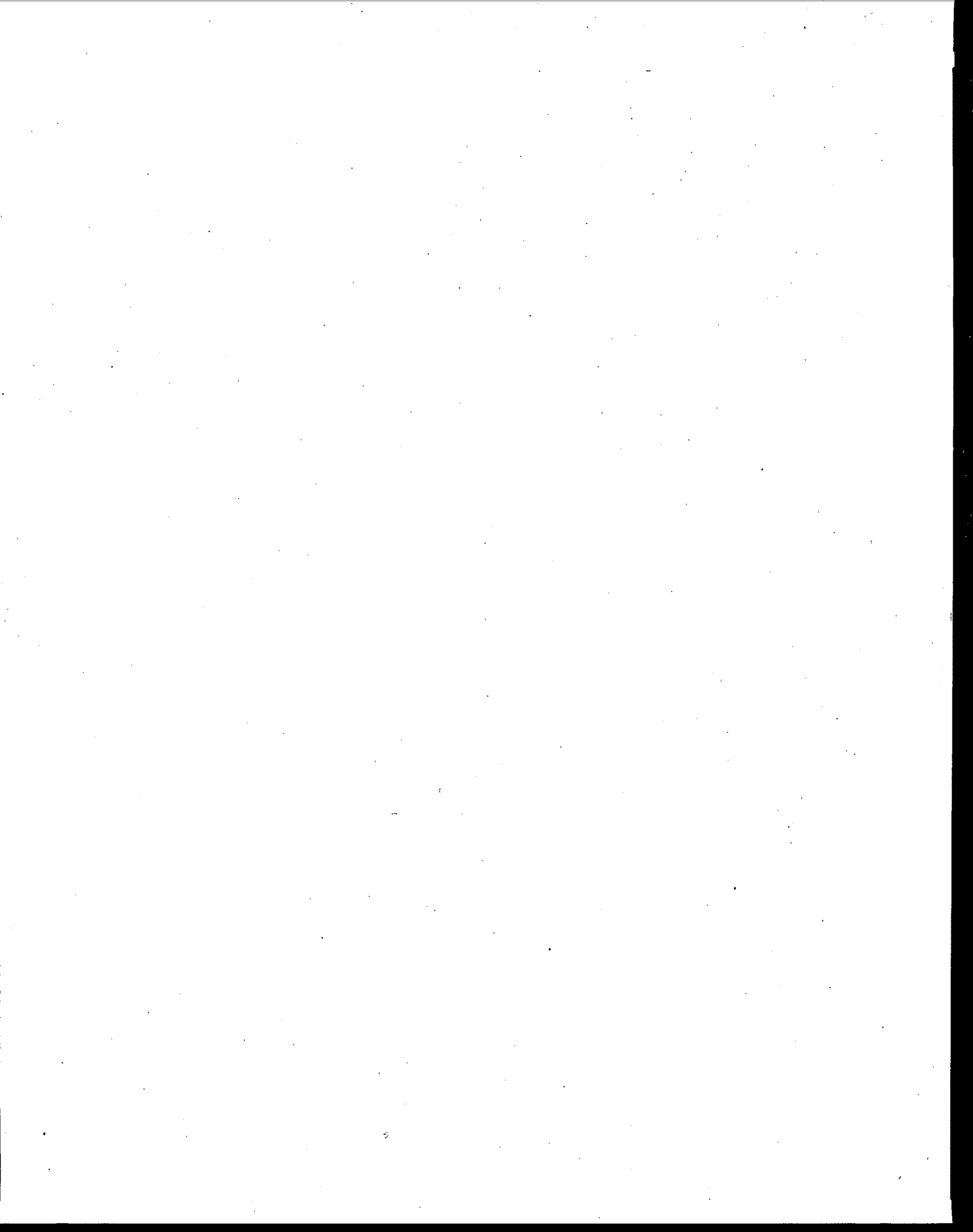
## **Conclusions and Recommendations**

In general, we have found GC/MI-IR spectrometry to be very useful for identifying SVOCs in a variety of environmental air sample extracts. In many cases the information obtained from the GC/MI-IR analyses supported tentative identifications made from preliminary GC/MS analyses. In cases where a definitive identification could not be made, the GC/MI-IR results often supplied enough information for a general compound classification to be made. In addition, the GC/MI-IR analysis often revealed unique information that could not easily be obtained by other existing analytical techniques. In particular, we have demonstrated the capabilities of GC/MI-IR to discriminate between compounds such as alkylbenzene positional isomers and PAH isomers, which are difficult to separate chromatographically and to distinguish by conventional GC/MS. Although absolute detection limits have not been determined, we have found that the minimum quantities of analyte needed for identifications by GC/MI-IR are very similar to those required by GC/MS in the scan mode. In practical terms, if a compound can be detected by scanning GC/MS, it is likely that an identifiable MI-IR spectrum of that component can be obtained on the GC/MI-IR system.

We recommend investigating the potential of interfacing the GC/MI-IR system to an MSD system to fully exploit the complementarity of the two techniques. We also recommend further evaluation of the quantitative capabilities of the GC/MI-IR technique and a thorough investigation to elucidate the sources of error in GC/MI-IR quantitative measurements.



**Figure 3.** MI-IR spectra of (A) a component of a carpet extract and (B)  $\epsilon$ -caprolactam reference standard.



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*The complete report, entitled "Gas Chromatography/Matrix Isolation-Infrared Spectrometry For Air Sample Analysis," (Order No. PB91-136 317/AS; Cost: \$23.00, subject to change) will be available only from:*

*National Technical Information Service*

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