



Project Summary

Gas Chromatographic/Fourier Transform Infrared Analysis of Trace Organics: Feasibility of Analysis After Collection of Organics on Tenax/GC Sorbent Cartridges

R. A. Palmer, J. W. Childers, and M. J. Smith

The combination of sorbent cartridge thermal desorption with capillary column GC/on-the-fly FTIR has been shown effective for the detection and identification of volatile organics in laboratory-generated mixtures, including the distinction between isomeric species, at the level of a few hundred nanograms per compound per cartridge. Traces of water desorbed from the cartridges must be reduced by the addition of a dryer unit between the desorption chamber and the GC column. Methods of lowering the detection and identification limits to less than 100 ng per compound per cartridge are proposed.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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 purpose of the project described in the full report was to evaluate the feasibility of using on-the-fly GC/FTIR to detect and identify volatile organics adsorbed on TENAX-GC cartridges. While the two analytical procedures of: (1) thermal desorption of TENAX-GC cartridges with

subsequent GC separation and (2) GC separation followed by FTIR detection have been separately utilized for the analysis of organic pollutants, it apparently has not been shown that TENAX-GC cartridge desorption can be successfully combined with GC/FTIR analysis. The primary goal of this project was to determine the feasibility of such a combination by analyzing well characterized laboratory-generated sample cartridges. Sample cartridges were loaded with realistic amounts (with respect to concentrations found in ambient samples) of various mixtures of organic compounds. Special emphasis was given to the identification of geometrical isomers. Instrumental problems addressed include removal of interferences due to water co-eluting with target compounds, spectral cleanup to facilitate library based identifications, and development of an analytical method to coordinate the various instrument subsystems necessary for precise analyses.

In principle, GC/FTIR should be complementary to GC/MS for the analysis of complex mixtures of volatile organic pollutants. Whereas GC/MS can often give molecular weights, provide information leading to an empirical formula, and provide some information about molecular structure, this information is in some cases insufficient to enable precise structural identification; this is particularly

true for geometrical isomers. GC/FTIR, on the other hand, is capable of identifying structural patterns of molecules and providing information about the functional groups present. By nondestructively probing the vibrational frequencies of various molecules it often affords a means of precise determination of structural formula.

Experimental

Samples for evaluation were prepared by exposing 1.35 g TENAX-GC cartridges to measured volumes of helium spiked with known concentrations of various target compounds (primarily volatile chloro-organics). These cartridges, containing typically 200-500 ng per compound, were thermally desorbed at 200°C and the target compounds subsequently trapped at -150°C using a Nutech* model 320 cartridge desorption, cryotrap and sample injection system. The cryotrapped compounds were then flashed through a Perma-Pure Nafion dryer and injected onto the temperature programmed capillary column (SE-54 fused silica WCOT) of a Varian 3700 gas chromatograph. Figure 1 shows a schematic diagram of the analytical system. The infrared spectral analysis of the GC eluent was carried out using the "on-the-fly" GC interface associated with the IBM-Bruker model 9195, N₂-purged FTIR spectrometer. A spectral resolution of 8 cm⁻¹ and range of 800-4000 cm⁻¹ were used. The typical 1 second residence time of a GC peak in the light pipe allows for the registration of 5 interferograms per peak. After standard transformation and background correction, IR spectra of eluted peaks were compared for identification to the Sadtler IRVAP-8 x 16 spectral library. For aid in locating peaks, the effluent from the light pipe of the GC interface was returned to the GC for FID analysis. A spectral resolution of 8 cm⁻¹ and range of 800-4000 cm⁻¹ were used. The typical 1 second residence time of a GC peak in the light pipe allows for the registration of 5 interferograms per peak. After standard transformation and background correction, IR spectra of eluted peaks were compared for identification to the Sadtler IRVAP-8 x 16 spectral library. For aid in locating peaks, the effluent from the light pipe of the GC interface was returned to the GC for FID analysis.

Results and Discussion

The relatively small amounts of water present in cartridge desorbed samples such as were used in this study pose no serious problem for a FID-monitored GC. However, even with the addition of the Nafion dryer unit, sufficient water remains in the GC eluent to be a significant problem for IR detection. The GC column used, although efficient for the separation of the relatively non-polar organic compounds of interest, tends to bleed polar compounds such as water over a wide

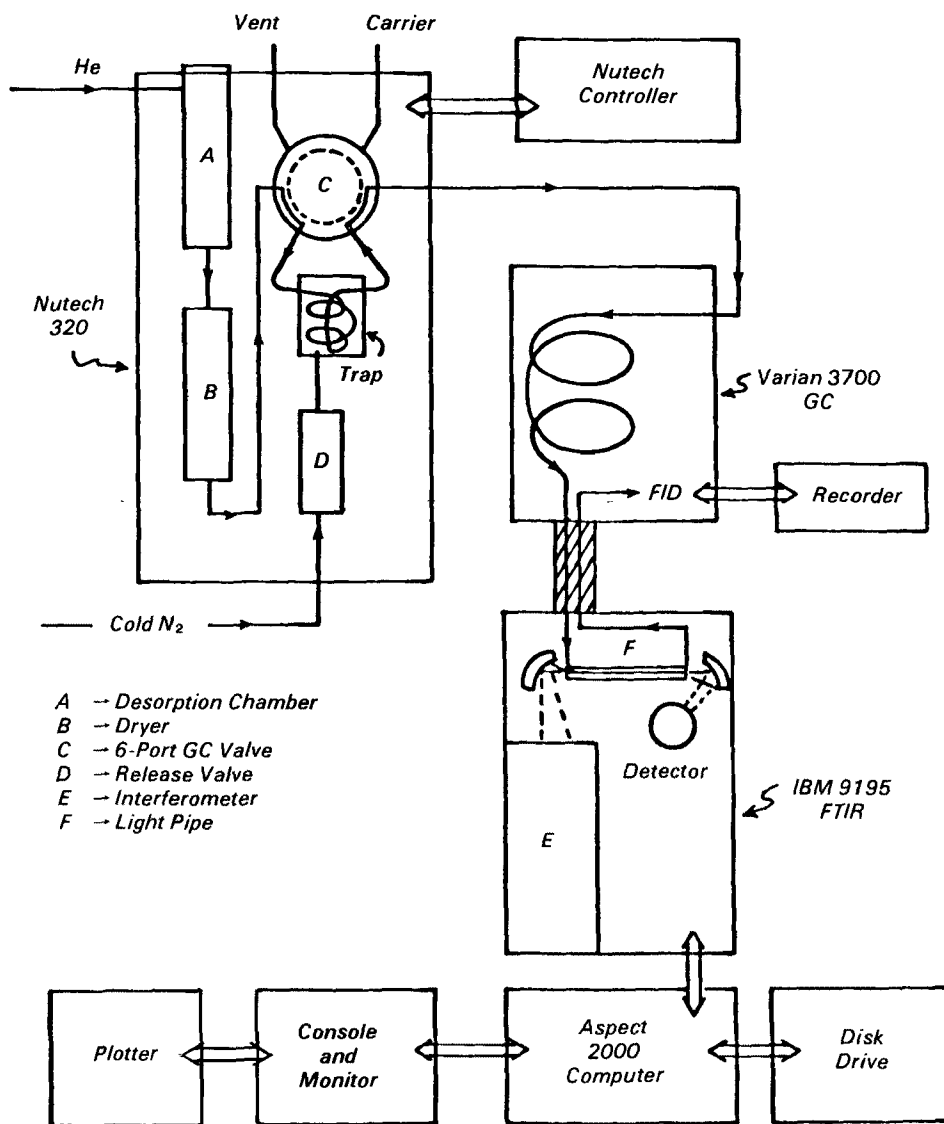


Figure 1. Bloc diagram of thermal desorption-GC/FTIR system.

region of the chromatogram. The result is a residual broad band observed in the FTIR generated real-time chromatogram (the Gram-Schmidt trace), as well as a background level of water which shows up in all spectra obtained. Fortunately, this background is easily corrected by subtracting from the spectrum the transform of summed interferograms obtained just before or after the peak interval. An example of this is shown in Figure 2. Because of the exact registration of the interferograms and their transforms (the spectra), this background correction is very efficient. Subsequent computer searches of the Sadtler IRVAP-8 x 16 library (8000 spectra), which is stored on

disk, consistently produced hits in agreement with the independently determined identity of the compounds in the test mixtures.

Of particular interest in the evaluation of the desorption-GC-FTIR system, are the results obtained for the mixture of several isomeric compounds as given in Table 1. The results of computer searches of the Sadtler IRVAP-8 x 16 library are also included in Table 1. The library search program returns the 10 best spectral matches and an associated "Hit Quality" number for each in the range 0 to 1000 (1000 indicates a perfect match). The column of Table 1 labelled "Hit Quality" gives a ratio where the first number

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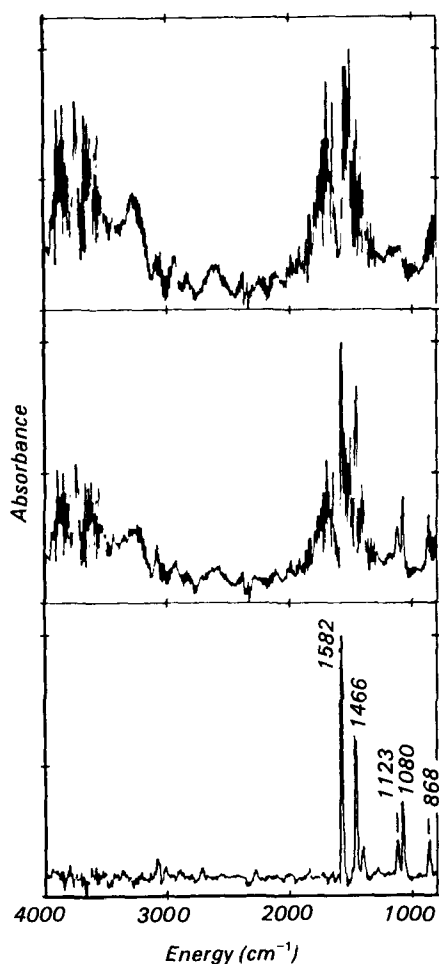


Figure 2. *m*-dichlorobenzene
 a) Absorption spectrum generated from adjacent baseline (background) correction.
 b) Uncorrected spectrum from peak interval.
 c) Corrected spectrum with peaks used for search identified.

Table 1. Geometrical Isomer Discrimination Mixture

Compound	Cartridge Loading (ng)	Peak No.	Search Hit No.	Hit Quality
<i>m</i> -xylene	381	1	*	
<i>p</i> -xylene	380			
<i>o</i> -xylene	389	2	10	262/434
<i>o</i> -chlorotoluene	477	3	7	380/500
<i>m</i> -chlorotoluene	473	4	1	444/444
<i>p</i> -chlorotoluene	471	5	2	658/676
<i>m</i> -dichlorobenzene	567	6	1	294/294
<i>o</i> -dichlorobenzene	575	7	1	310/310

**m*- and *p*-xylene co-elute. See text.

indicates "goodness of fit" of the subject spectrum to the correct library spectrum, and the second number indicates "goodness of fit" of the subject spectrum to the #1 ranked (but possibly incorrect) match.

In the results summarized in Table 1 it should be noted that each of the last four compounds eluted was identified from its background corrected spectrum by routine search of the IRVAP library as either the first or second best "hit." The correct identities of the third and fourth compounds were also included in the best 10 hits, though these two results would certainly not have independently supported correct identification. Because of the co-elution of *m*- and *p*-xylene (peak 1), these two compounds could not be identified by routine search of the Sadtler library. (The combined spectrum is not recognizable as any individual compound.) In order to identify successfully these two compounds a *bona fide* reference spectrum of one or the other isomer should be subtracted from the combined experimental spectrum. The residual spectrum could then be submitted to the search routine with expectation of successful identification of the other isomer. A user generated library containing the reference spectra of *m*- and *p*-xylene must be created for this purpose.

It should also be noted that the search results in Table 1 were obtained without using any restrictions on the peak picking program of the search routine, nor was any smoothing applied to the spectra before submitting them to the search routine. In addition it should be emphasized that the library contains 8000 spectra of a wide variety of compounds and that these were obtained using different equipment (although the resolution is the same). In several of the searches it is clear that relatively strong

spurious (noise) peaks have been identified in the peak picking routine which would be eliminated by reasonable increase in the peak picking threshold. The search of a more selective library of spectra generated using the same GC/FTIR instrument could be expected to yield more consistently low hit numbers and higher hit qualities than the search of the standard Sadtler library. Information on retention time, compound volatility range and column material would eliminate many compounds in the spectral library from consideration.

Another serious problem inherent in the method as executed in this study is that it is difficult to identify peaks in the Gram-Schmidt trace because of the pervasive water background. Useful spectra can be obtained from the transform of co-added interferograms recorded during the passage of a compound through the light pipe even when the corresponding peak is effectively obscured by the background in the Gram-Schmidt trace. Since such peaks are usually clearly identified in the (subsequent) FID detected chromatogram, it appears that modification of the equipment so as to allow the use of the FID to trigger the saving of interferograms (rather than using the Gram-Schmidt algorithm for this purpose) would yield a significant improvement in, not only the speed of the method, but also its reliability and detection limits.

Conclusions

The combination of sorbent cartridge (TENAX-GC) thermal desorption with capillary column GC/on-the-fly FTIR has been shown effective for the detection and identification of volatile organics in laboratory-generated mixtures, including the distinction between isomeric species, at the level of a few hundred nanograms per compound per cartridge. The use of a dryer element immediately following the desorption unit has been shown essential for selective removal of traces of water also desorbed from the TENAX-GC, which otherwise seriously degrade the detection limits. The necessity of the use of the dryer element restricts the use of the method to non-polar compounds. Detection limits for the system as currently configured are determined by the ability to observe peaks in the Gram-Schmidt (real-time) FTIR chromatogram. Potential detection and identification limits are less than 100 ng per compound per cartridge, or sub-ppb levels of detection for 20L air samples drawn through the sorbent cartridges. Hardware and software improve-

ments designed to achieve these limits and also retain semi-automatic data collection are described below.

Recommendations

From the results obtained to this point, several additional improvements to the method can be recommended which will reduce the degree of operator intervention required, decrease analysis time, and significantly lower detection and identification limits.

1. A user-generated library of spectra of target compounds should be established to supplement the Sadtler library. These spectra should be obtained using the complete desorption-GC/FTIR system, from authenticated mixtures loaded at the level of *ca.* 1000 ng per compound per cartridge.
2. Changes in the hardware and/or software should be developed which will use the FID to trigger the saving of interferograms, rather than using the Gram-Schmidt algorithm.
3. An objective protocol for raising the sensitivity of the peak-picking program of the library search should be developed. Factors such as retention time, column material and range of compound volatilities need to be used to exclude subgroups of compounds in the spectral library.

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W. A. McClenny is the EPA Project Officer (see below).

The complete report, entitled "Gas Chromatographic/Fourier Transform Infrared Analysis of Trace Organics: Feasibility of Analysis After Collection of Organics on Tenax/GC Sorbent Cartridges," (Order No. PB 86-118 932/AS; Cost: \$11.95, subject to change) will be available only from:

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