Chapter 7. Gas chromatography with ultraviolet detection for the analysis of tholins

7.1. Introduction

The development of spaceflight instrumentation is challenging, due to the restrictions on power, weight, and volume that space probes necessitate. For the analysis of organics, few systems can compare to GC-MS in their ability to identify the components of complex mixtures. While GC-MS systems have been developed for spaceflight purposes, they are especially difficult to design in a way that satisfies the requirements of power, weight, and volume. The major obstacle is the necessity of vacuum for the mass spectrometer system, which requires a bulky and power-hungry pumping system.

This chapter describes an unusual instrument, a gas chromatograph coupled to a gas-phase far ultraviolet spectrometer. Examination of the gas-phase ultraviolet spectrum would allow for functional group identification of the separated compounds, although it would not necessarily permit precise identification. As well, such a system would not require vacuum, and could be miniaturized relatively easily. Since the technique is non-destructive, it could also serve as a backup detector for a more traditional mass spectrometer detector. The instrument, with minor modifications, has also been used to detect organonitrate explosives (see Appendix A).

The coupling of gas phase ultraviolet absorption with gas chromatography has been practiced sporadically for the past 40 years. Kaye reported the first GC-UV system in 1962 [Kaye, 1962], which used ultraviolet absorption at 170 nm for the analysis of a chromatographic separation of gasoline. GC-UV systems have since been used for the analysis of wine [Cedron-Fernandez*, et al.*, 2002], indoor dust [Lagesson*, et al.*, 2000a], and proposed as a means for functional group analysis [Lagesson*, et al.*, 2000b].

We describe a GC-UV system, and its use in the identification of the products of low-temperature pyrolysis of tholins. The data obtained is compared to the data obtained by GC-MS. The spectra of a number of reference compounds have also been obtained for comparison. As well, these spectra may be useful in modeling the atmospheric properties of Titan, as the gas-phase far ultraviolet spectra of many small nitriles and amines are unknown.

7.2. Experimental

A block diagram of the experimental apparatus is shown in Figure 7.1. The laboratory-constructed pyrolyzer is shown in Figure 7.2. A 3 mm OD borosilicate glass tube is packed with a small wad of glass wool, a few milligrams of tholin, and then another wad of glass wool. The glass tube is wrapped with several turns of nichrome wire in the area of the tholin, and sealed into the injector of the gas chromatograph with a graphite ferrule and an 1/8“ Swagelok fitting. For pyrolysis, a flow of 50 mL/min of helium is passed through the pyrolyzer, and a current of 2 A is passed through the Nichrome wire for 15 s. This heats the sample to 220 °C, as determined by placing a thermocouple in the pyrolyzer and heating as above. The current is switched off, and the helium flow is stopped. The gas chromatograph program then proceeds normally. The gas chromatograph (SRI Model 8610C) is connected to a heated absorption cell via a heated stainless steel transfer line, usually held at 100 °C. The cell consists of two aluminum blocks supporting a quartz tube (3 mm OD) between them, with silica windows on either side. The tube serves as both a light pipe and a conduit for the gas chromatograph effluent. The cell has a pathlength of ~6 cm, and is typically heated to 100 °C. Residence time in the cell is approximately 3 s, so no peak broadening due to the cell is expected.

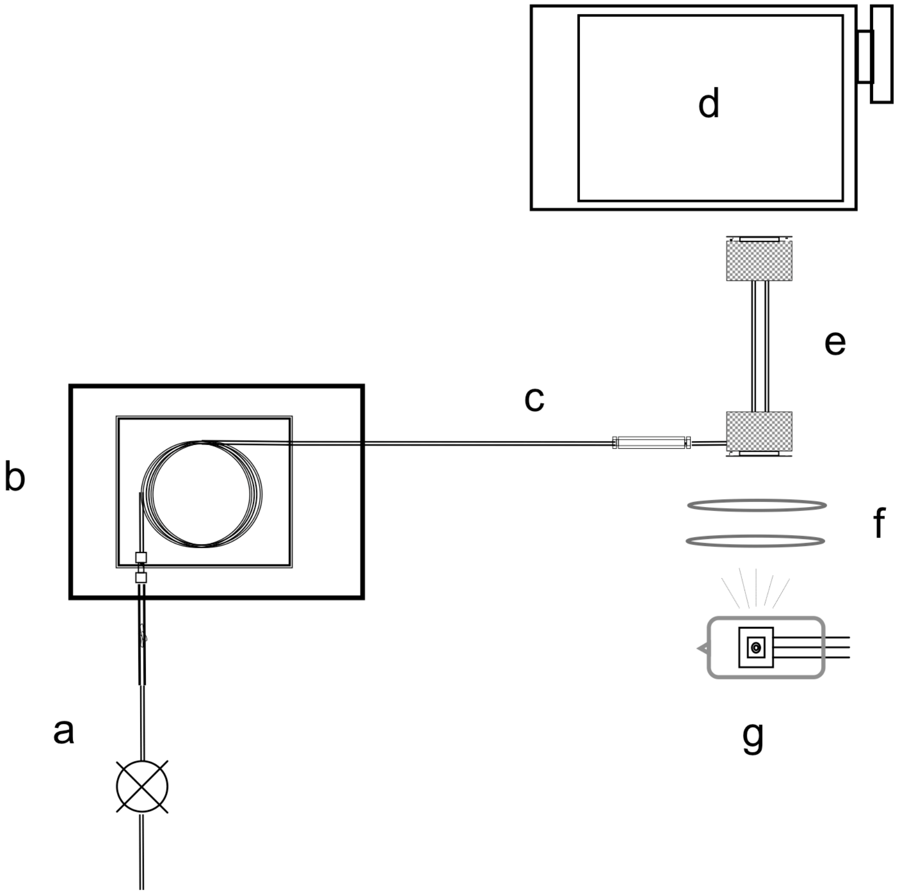

Figure 7.1. Pyrolysis-GC-UV system. a) pyrolyzer, b) SRI 8610 gas chromatograph, c) transfer line, d) Chromex 250is spectrometer, e) absorption cell, f) silica lenses, g) deuterium lamp.

The light from a 30 W deuterium lamp (Oriel 63163) is coupled into the cell using silica lenses. Unfocused light exiting the cell is directed into a Chromex 250is imaging spectrograph equipped with an Apex SPH-5 CCD detector. The resolution of the system is approximately 0.5 nm. The entire optical path, including the spectrometer, is purged with nitrogen to allow operation below 200 nm. Spectra from 185-240 nm are acquired approximately every 1.5 seconds, with an integration time of 1 s.

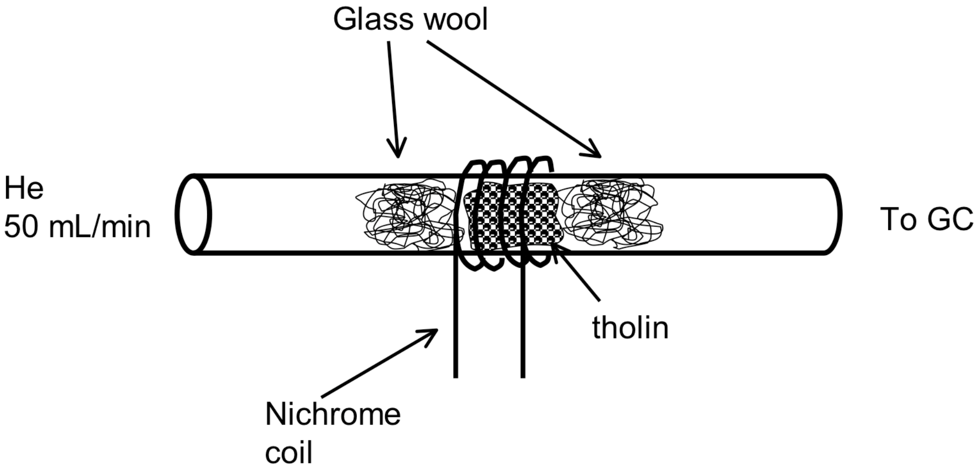

Figure 7.2. Lab-built low temperature pyrolyzer.

The gas chromatograph uses a 100% methyl polysiloxane column (MXT-1 15m × 0.53mm × 5μm film) with on-column injection. The temperature of the GC oven was ramped from 25 °C to 250 °C at 10 °C/min. Helium was used as the carrier gas with a source pressure of 10 psig.

GC-MS chromatograms were obtained in the following manner. In order to replicate the pyrolytic conditions in our lab-built pyrolyzer, the injector of the gas chromatograph was set to a temperature of 220 °C. Approximately 1 mg of tholin was dissolved in 100 uL dichloromethane, and 1 uL of this solution was injected into the gas chromatograph, a Varian 3400 CX equipped with a Varian Saturn 2000 mass spectromter detector. The column was a DB5 capillary column. The temperature program was the same as that used above. Although the column and injection conditions are different, by keeping the temperature program the same as that used with the GC-UV system, we can make reasonable correlations between the data obtained by each method.

7.3. GC-UV of tholin pyrolysis products

Figure 7.3 is the chromatogram obtained by GC-MS. Peaks were identified by comparison with mass spectra from the NIST Chemistry WebBook library [Linstron and Mallard, 2005]. The following compounds were observed: 1) butyronitrile, 2) isobutyronitrile, 3) pentanedinitrile, 4) 2-methyl-2-butenenitrile, and 5) hexanedinitrile. The compounds are primarily alkyl nitriles and dinitriles, with some alkenes as well. These products are consistent with the results from other analyses of pyrolysis products [Coll*, et al.*, 1998]; [Ehrenfreund*, et al.*, 1994]; [Israel*, et al.*, 1997]; [Pietrogrande*, et al.*, 2001]. Examination of the spectra of some of the unidentified compounds show many of the same fragments as other, earlier eluting peaks, but with differing intensities, suggesting that they are structural isomers of the earlier peaks. For instance, the starred peaks in Figure 7.3 all have similar molecular ion masses and fragmentation spectra as peak 5, and so are identified as isomers of hexanedinitrile.

Figure 7.4 is a three-dimensional chromatogram of the products of the pyrolysis of tholin (sample CH154) obtained by GC-UV. At least a dozen distinct peaks are visible. The peaks are rather broad; this is due to the pyrolyzer, which delivers analyte to the column over a relatively long period of time (15 s). This slow injection results in broad peaks. The initial region of very high absorbance corresponds to the period of time when the sample is being pyrolyzed. An examination of the spectrum of this region shows that is composed mostly of ammonia, which is not retained by the column. Ammonia has been shown to be released in large quantities by the tholin when heated (Chapter 4).

The spectra corresponding to selected peaks in the chromatogram are shown in Figures 7.5-7.7. Figure 7.5 and 7.6 are the spectra corresponding to peaks at

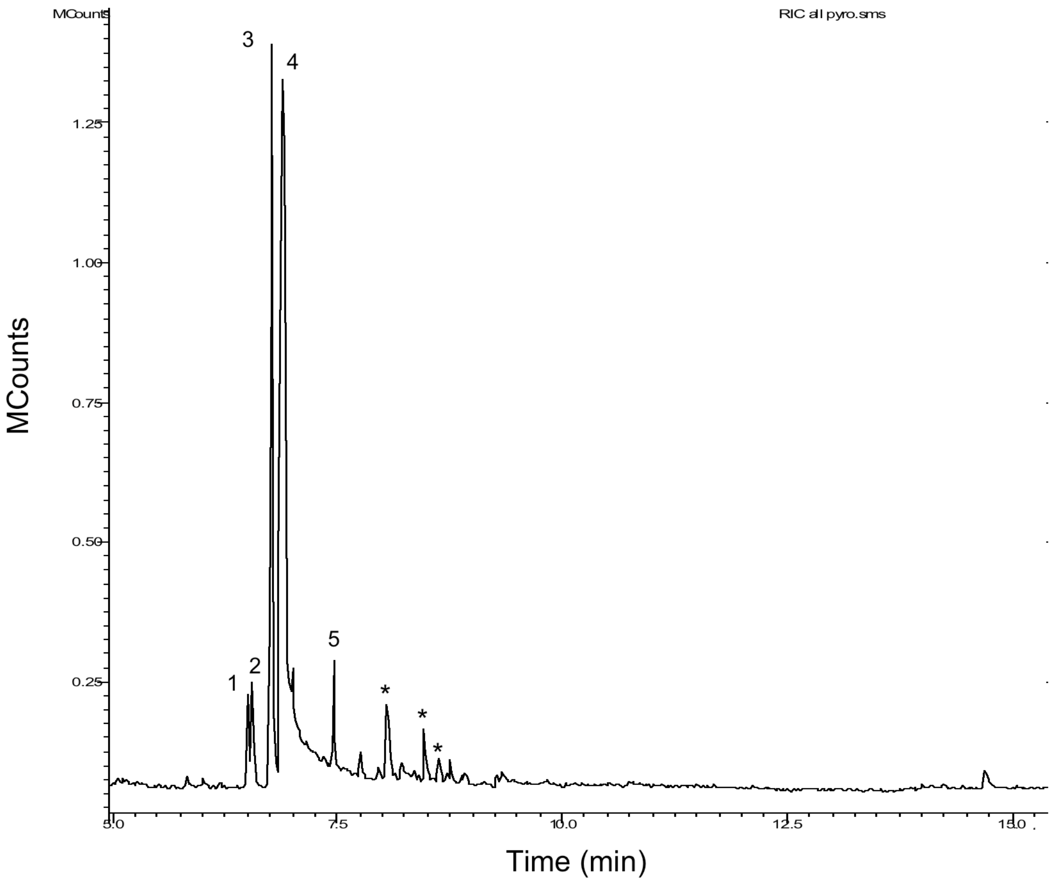

Figure 7.3. GC-MS chromatogram of the low temperature pyrolysis products of tholins.

approximately 90 s and 125 s, respectively. The peaks are broad, with structure superimposed onto the peaks at 125 s. The superimposed structure is identical to the vibrational structure present in the absorption spectrum of ammonia. This is the result of the tail of the very strong ammonia peak at the beginning of the chromatogram.

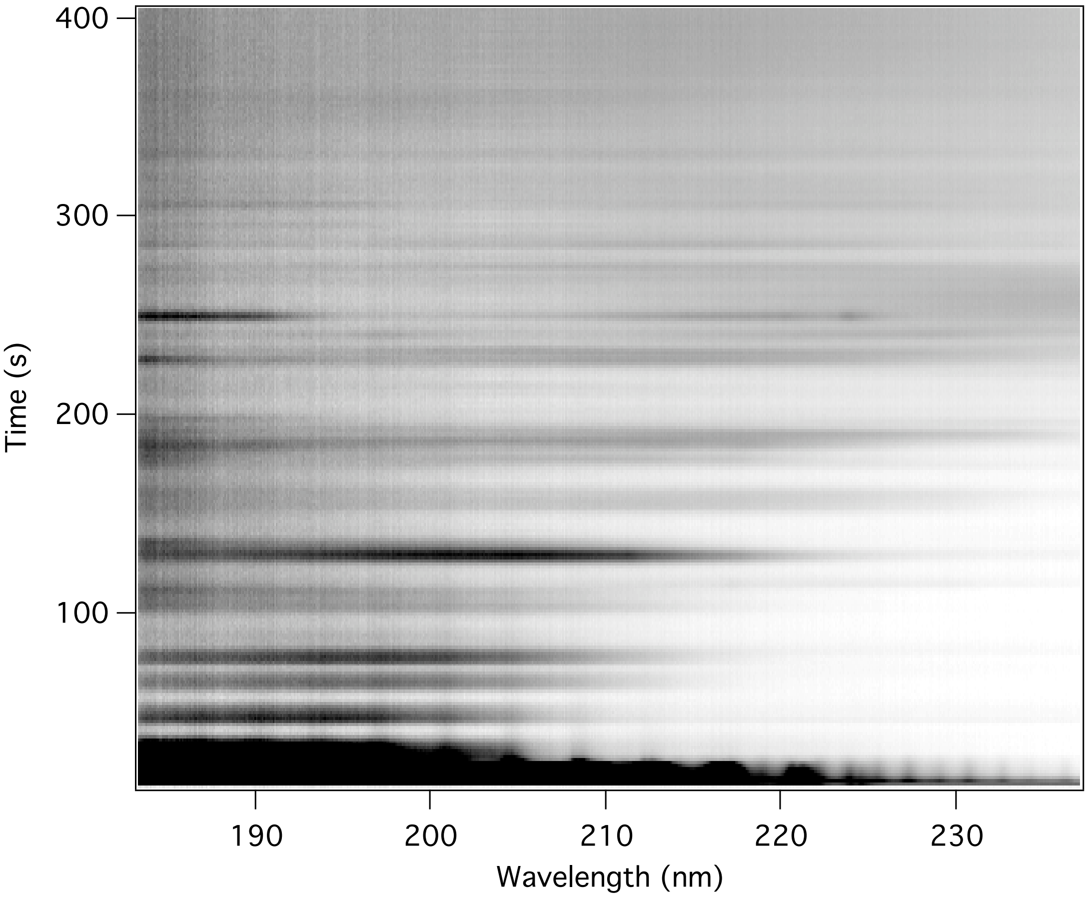

Figure 7.4. 3-D GC-UV chromatogram of tholin pyrolysis products.

Although little information on the gas-phase far ultraviolet spectra of nitriles is available, the broad peaks are consistent with the literature. Nitriles have a relatively weak $\pi \rightarrow \pi^*$ transition at around 200 nm [Robin, 1975].

The most interesting spectrum is that of the compound that elutes at approximately 250 s. The spectrum has a broad peak peaking below 190 nm, and another peak with some vibrational structure around 220 nm. For comparison, the spectrum obtained from the injection of 6-hexenenitrile is shown in Figure 7.9. The qualitative similarity of the two spectra in the region around 220 nm suggests that this peak corresponds to an alkene nitrile (not necessarily 6-hexenenitrile), as seen in the GC-MS data.

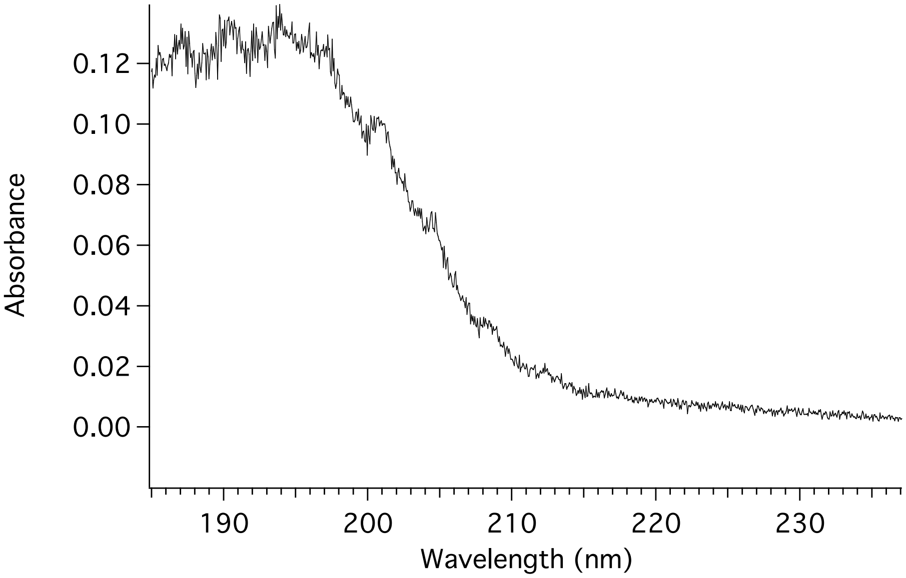

Figure 7.5. Spectrum of the peak eluting at 90 s.

The spectra from some amines and a simple alkyl olefin are shown in Figures 7.8 and 7.10-7.12. Although none of these compounds are seen in the pyrolysis data obtained by GC-MS, their distinctive spectra would enable their identification if present in another complex mixture. Even though no aromatics are seen in these low temperature pyrolytic reaction, high temperature pyrolysis does yield a number of aromatic compounds [Coll, *et al.*, 1998]; [Ehrenfreund, *et al.*, 1994]; [Israel, *et al.*, 1997];

[Pietrogrande*, et al.*, 2001]. These would also be easily distinguished by GC-UV, since they have characteristic vibrational structure in the 230-250 nm region.

7.4. Conclusions

The products of low-temperature pyrolysis of tholins have been analyzed by GC-UV. The spectra obtained with the GC-UV system are consistent with the compounds determined to be present by GC-MS. Low temperature pyrolysis produces mainly alkyl nitriles and dinitriles, with some alkene nitriles. Although amines and aromatics are absent, they would also be identifiable by their ultraviolet spectra.

A GC-UV system would be a useful addition to a probe whose mission is to explore the organic chemistry of other worlds, especially Titan. Such a system could be made small, lightweight and low-power, making it ideal for spaceflight situations. Although it would not provide exact identification of compounds, functional group identification is possible, and since the technique is non-destructive, GC-UV could serve as a backup to a more traditional GC-MS system.

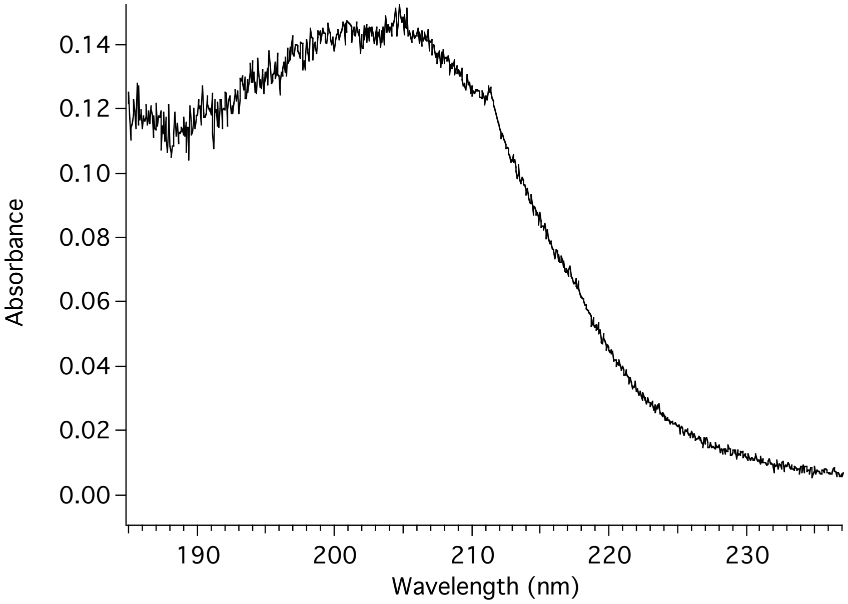

Figure 7.6. Spectrum of the peak eluting at 125 s.

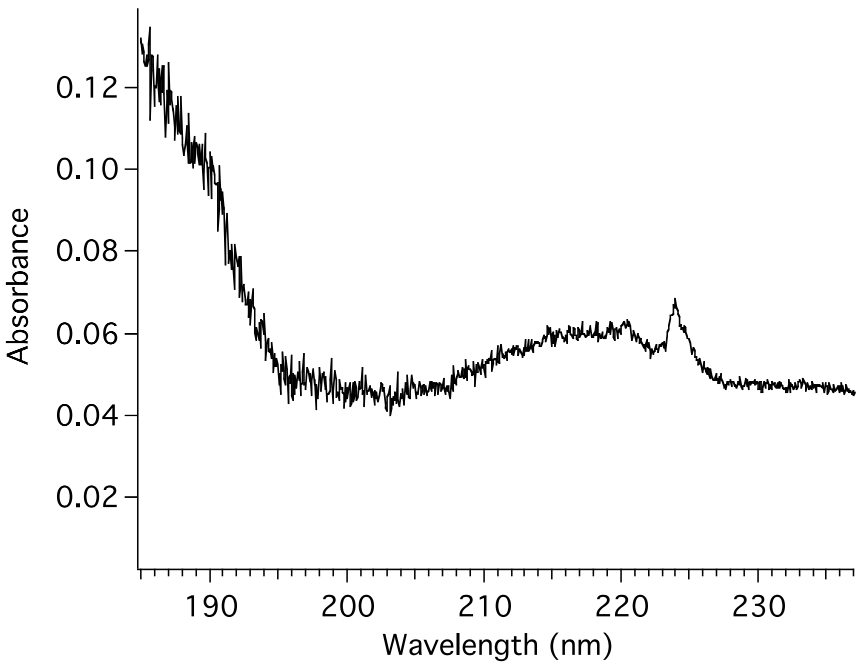

Figure 7.7. Spectrum of the peak eluting at 250 s.

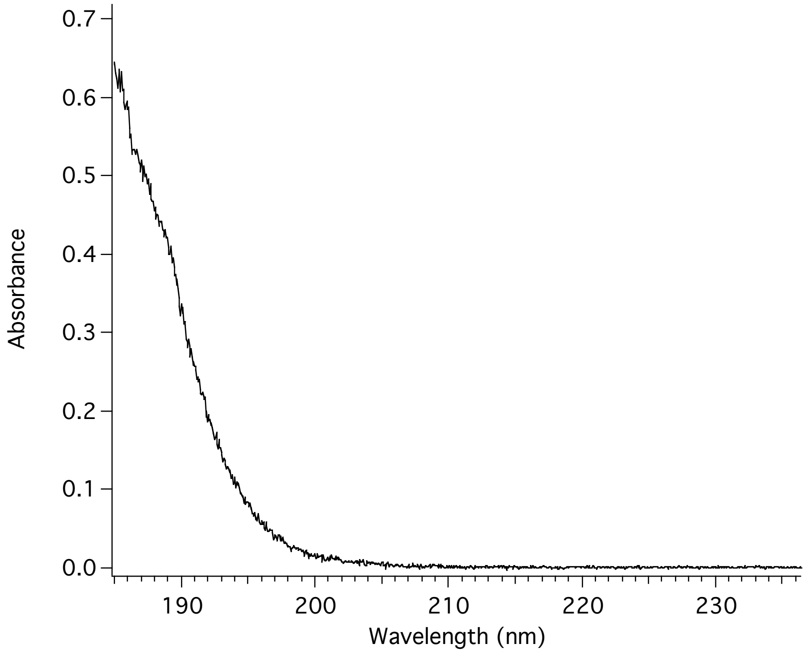

Figure 7.8. Gas-phase ultraviolet spectrum of 1-hexene.

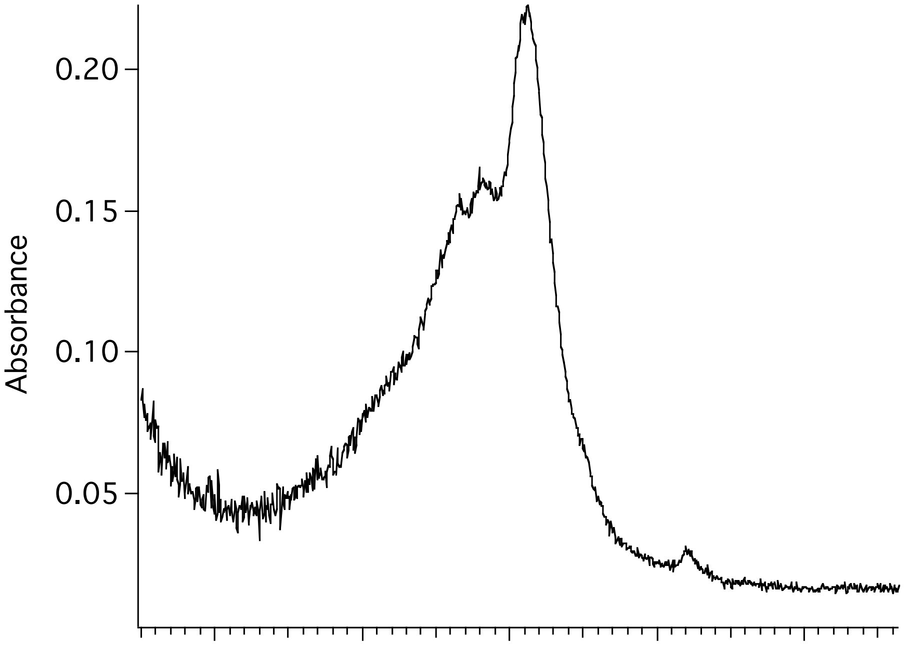

Figure 7.9. Gas-phase ultraviolet spectrum of 5-hexenenitrile.

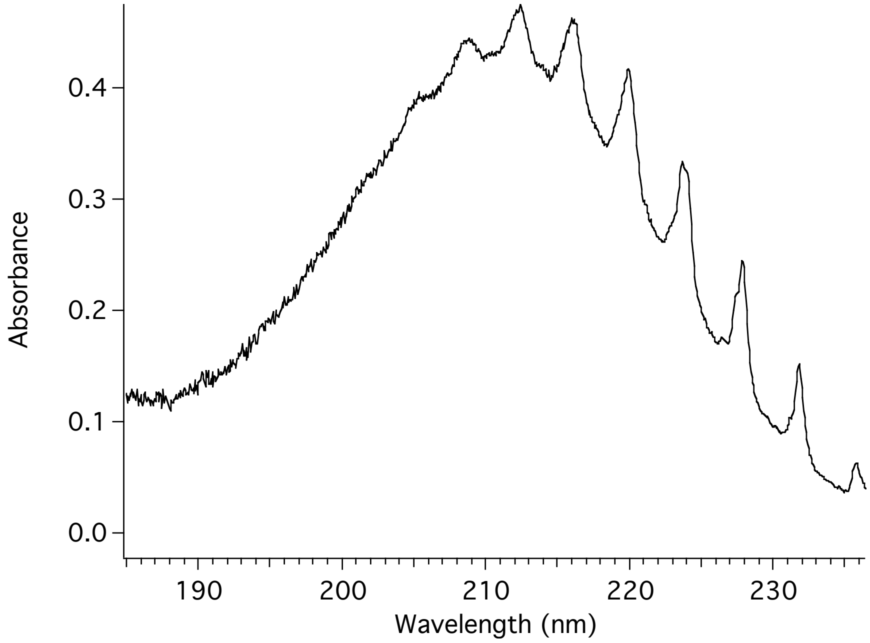

Figure 7.10. Gas-phase ultraviolet spectrum of tert-butylamine.

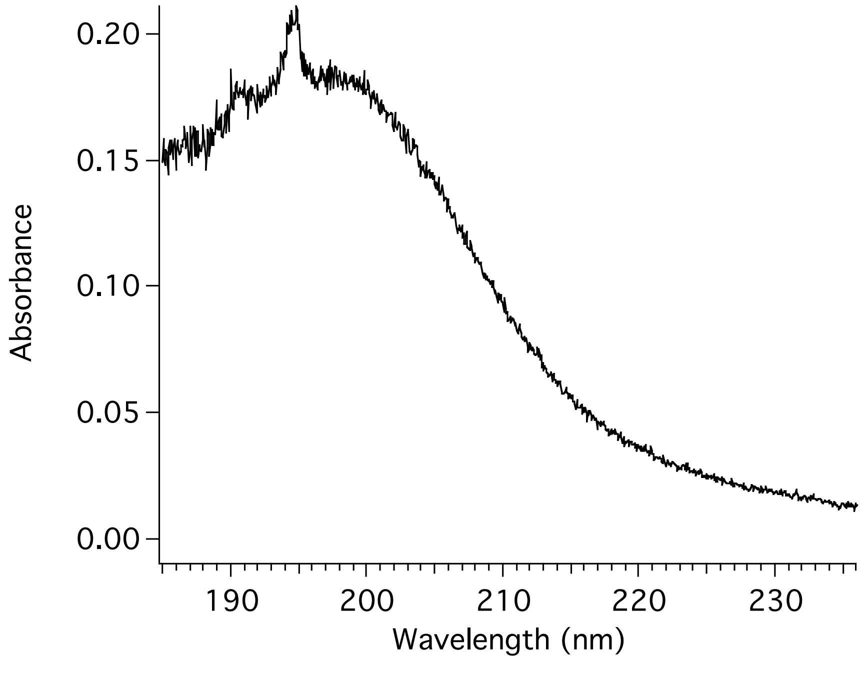

Figure 7.11. Gas-phase ultraviolet spectrum of diethylamine. The peak at 194 nm is due to interference from acetone.

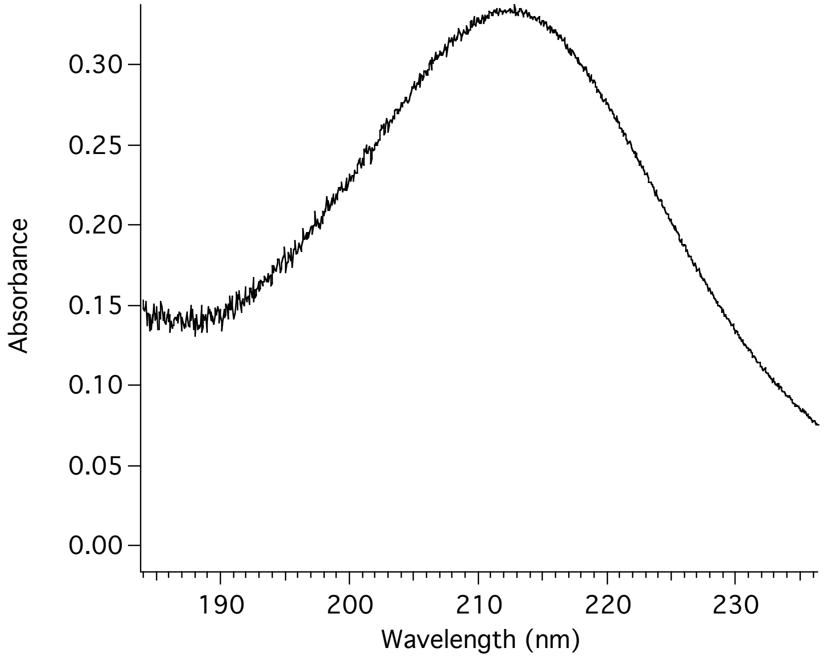

Figure 7.12. Gas-phase ultraviolet spectrum of triethylamine.

7.5. References

Cedron-Fernandez, T., et al. (2002), Separation and determination of volatile compounds in synthetic wine samples by gas chromatography using UV-visible molecular absorption spectrometry as detector, *Talanta*, *57*, 555-563.

Coll, P., et al. (1998), Review and latest results of laboratory investigations of Titan's aerosols, *Origins of Life and Evolution of the Biosphere*, *28*, 195-213.

Ehrenfreund, P., et al. (1994), Analytical Pyrolysis Experiments of Titan Aerosol Analogs in Preparation for the Cassini Huygens Mission, *Life Sciences and Space Research XXV (4)*, *15*, 335-342.

Israel, G., et al. (1997), The Aerosol Collector Pyrolyser (ACP) Experiment for Huygens, in *Huygens: Science, Payload and Mission*, ESA Publications Division, Noordwijk, The Netherlands.

Kaye, W. (1962), Far-Ultraviolet Spectroscopic Detection of Gas Chromatograph Effluent, *Analytical Chemistry*, *34*, 287.

Lagesson, H. V., et al. (2000a), Qualitative determination of compounds adsorbed on indoor dust particles using GC-UV and GC-MS after thermal desorption, *Chromatographia*, *52*, 621-630.

Lagesson, H. V., et al. (2000b), Identification of compounds and specific functional groups in the wavelength region 168-330 nm using gas chromatography with UV detection, *Journal of Chromatography A*, *867*, 187-206.

Linstron, P. J., and W. G. Mallard, eds,. (2005), *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute od Standards and Technology, Gaithersburg, MD.

Pietrogrande, M. C., et al. (2001), Analysis of complex mixtures recovered from space missions - Statistical approach to the study of Titan atmosphere analogues (tholins), *Journal of Chromatography A*, *939*, 69-77.

Robin, M. B. (1975), *Higher Excited States of Polyatomic Molecules*, Academic Press, San Francisco.