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EVALUATIONS OF AN ENHANCED TOTAL HYDROCARBON ANALYZER WITH COMPLEX MIXTURES OF VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

From the earliest manned missions, the volatile organic compound (VOC) content of spacecraft air has been a concern because of a much greater potential for contamination than air in most terrestrial settings. First, the volume of air is small compared to the mass of man-made materials comprising the interior furnishings of the spacecraft. These man-made materials offgas VOCs trapped during manufacture. Second, the nigrogen fraction of the air is recycled. Any VOCs not scrubbed out with charcoal filters or aqueous condensate (mainly water expired by the crew) will accumulate in the air. Third, the crew emits metabolic VOCs. Fourth, experimental payloads can also offgas or accidentally release a VOC; in fact a major organic constituent of the atmosphere is the disinfectant isopropanol released from swabs used in medical experiments.

The Enhanced Total Hydrocarbon Analyzer (ETHA) has been described in another paper in these proceedings (Hinton, 1995). The instrument was built by Graseby Dynamics to NASA requirements for real time monitoring of VOCs in spacecraft atmospheres. The ETHA is the first instrument resulting from a developmental program that will culminate in an operational monitor for the International Space Station. This first instrument is an important step in NASA's efforts to maintain crew health during spaceflight. Previously, NASA has measured VOCs with archival samples collected in evacuated canisters analyzed on the ground after a mission. On the space station, archival sampling will no longer be feasible and real time monitors such as the ETHA and its successors will become the standard. Trials using the ETHA will provide the first opportunity for comparing archival and real-time results and for developing the techniques of real-time spacecraft air monitoring.

The analytical requirements for the ETHA are challenging. The variety of VOC sources mentioned above means the instrument must detect chemicals with various functionalities. Currently, the NASA Toxicology Laboratories target 66 compounds for analysis in archival samples and others are detected occasionally. Compounds must be identified without false positives, and the identification routines must be capable of recognizing that an unidentified compound has been detected. The instrument must be sensitive. NASA has set exposure limits (spacecraft maximum allowable concentrations, or SMACs) for many VOCs (Garcia and James, 1995). Most of these are in the low ppm or high ppb range. Since the crew is exposed continually and is also participating in physiological experiments on the effects of weightlessness, a monitor needs to be able to detect concentrations much lower than the SMACs. The monitor must also quantify its results with a precision appropriate to toxicological needs. Fortunately, the required precision for these biological measurements is relatively low, ca. 50%. Quite a different requirement is the need to rapidly assess the overall burden of VOCs in the atmosphere and to detect leaking VOCs. Finally, although not directly related to analytical requirements, the instrument must be simple to operate and capable of functioning under what are essentially field conditions.

ETHA design solutions to meet the analytical requirements include a gas chromatograph (GC) to provide selectivity, a solid-sorbent preconcentrator designed to extend sensitivity to the ppb range, and an ion mobility spectrometric (IMS) detector to identify target compounds and recognize unknowns. Functioning together, these subsystems are a GC/IMS for target compound analysis. In addition, a membrane inlet provides an air sample directly

to the IMS detector for assessing the total burden of VOCs. We designated this capability "total hydrocarbon analysis (THA)." These features and many others required to support them have been assembled into an instrument that is undergoing its initial analytical tests now.

This paper reports the results of tests to date (July 1995), which are being conducted prior to delivery to Johnson Space Center. The purpose is to assess the potential of the instrument to meet the performance requirements of selectivity, sensitivity and precision. Thus, the maximum number of compounds have been analyzed and the operating parameters have been kept within narrow ranges.

EXPERIMENTAL METHOD

The preconcentrator, GC, and the IMS detector are described in another paper in this proceedings (Hinton, 1995). All transfer lines between the inlet, preconcentrator and GC column are held at 80°C. The IMS detector is held at 100°C.

Compounds tested

All the compounds tested to date give IMS responses in the positive mode. Samples are presented to the ETHA in dry air in one of two ways. Ethyl acetate (5 mg/m^3) is generated using a permeation tube in a Graseby Dynamics gas generator. Mixtures of components are made by dissolving reagent grade chemicals in 1,1,2-trichloro-1,2,2-trifluoroethane, and injecting a suitable quantity of this solution into a glass jar, which is presented to the ETHA during the 100 sec. sampling time. The compounds tested are shown in Table 1.

Table 1
ETHA Test Compounds

Test Compound (Elution Order)	Concentration (mg/m^3)
Acetaldehyde	0.5
Methanol	0.5
Ethanol	5
Acetone	1
Isopropanol	5
n-Butanol	5
t-Butanol	5
Hexane	5
Benzene	0.1
Ethyl acetate	5
Pinacolone	(IS)*
Toluene	3
Xylenes (o,m,p)	10
Hexamethylcyclotrisiloxane	10
2-Butoxyethanol	1
4-Hydroxy-4-methyl-2-pentanone	1

*Internal Standard

Gas Chromatographic Analysis

The GC column is a 60 m by 0.5 mm i.d. stainless steel capillary with a 1.5μ film thickness of 5% phenyl/95% methyl silicone stationary phase chemically bound to the steel. The carrier gas is ultrapure nitrogen flowing at 3 ml/min.

The analytical procedure begins by drawing a 100 ml sample through the inlet onto the preconcentrator. After the sample is collected, the preconcentrator is simultaneously purged of oxygen and given a dose of internal standard (pinacolone) from a permeation tube. Next, switching a 6 port Valco™ valve causes the carrier gas to flow through the preconcentrator and into the column. Simultaneously, the preconcentrator is heated to 275°C for 5 min. and is then raised to 325°C for 0.5 min. The sample is thus transferred to the head of the GC column which is held at 40°C throughout the transfer. The Valco valve is then switched back to its original position and data acquisition begins. The column is held at 40°C for 600 sec., then raised to 150°C at 6°C/min. and held there until 2600 sec. Data acquisition is then halted and the column temperature is returned to 40°C.

Total Hydrocarbon Analysis

An unseparated sample of VOCs in air is obtained through a thin silicon rubber membrane. Pressing a button on the front of the ETHA routes an air sample past one side of the membrane. The VOCs partition across the membrane and are entrained in a clean, dry air flow that carries them directly to the IMS detector. Sampling ceases when another front panel button is pressed

Data Reduction

Data reduction is accomplished using four windows (Figure 1). The lower left window is a gas chromatogram constructed from the amplitude (*y*-axis) of the reactant ion peak (RIP). Both positive and negative mode RIPs can be displayed. Since detecting an eluting compound reduces the RIP amplitude, negative peaks are displayed. Product ion peaks can also be selected for detection of target compounds. The upper left and lower right windows display positive and negative mobility spectra respectively. The upper right window records the positions of cursors in the other three windows. Moving the cursor in the chromatographic window selects the mobility spectra collected at that particular elution time. Moving the cursors in the spectral windows gives drift times and amplitudes of peaks. THA results can be displayed analogously, but instead of chromatographic elution time, the data is presented for the time of acquisition.

RESULTS AND DISCUSSION

A chromatogram of 5 mg/m^3 ethyl acetate is shown in Figure 2. The largest peak is ethyl acetate. The peaks on the left are ethanol and acetone respectively, which are sometimes sampled inadvertently from the air of the laboratory. The peak to the right is the internal standard. Note that the most important requirement of an internal standard is met; the quantity of standard is about the same as that of the analyte. Even allowing for the widely differing response factors expected from an IMS detector, the requirement seems to be met. The ethyl acetate mobility spectrum shown is taken at the tip of the GC peak. It shows the RIP (left), monomer and dimer peaks. Along the bottom of the chromatogram is a second trace, which was made by defining a window at the drift time of the dimer. Since none of the other three compounds in the chromatogram generate product ions at this particular drift time, a selective detection has occurred. Significantly, the sensitivity of the IMS detector is adequate for the concentrations of interest. Estimating from the baseline noise and stray peaks, a concentration of 10-20% of 5 mg/m^3 should be detectable. Higher concentrations should also be detectable, because the RIP is not depleted.

A larger mixture with a wider range of volatilities is shown in Figure 3. The most volatile components have quite narrow peaks considering the injection method. Usually when desorbed compounds are reconcentrated, the head of the column is cryogenically cooled. This is not possible in an instrument designed for spaceflight use. The lower trace in Figure 3 shows the internal standard dimer, which has an unusually long dimer drift time (Figure 4, ca. 7.3 ms). When interpreting the chromatogram of more complex mixtures, this feature helps locate the standard reliably. The response to a saturated hydrocarbon, hexane (Figure 5), is another indication of the wide selectivity of the IMS detector. Benzene, at 2% the concentration of hexane, gives a much lower response that has not yet been reliably identified in mixtures. The response to 4-hydroxy-4-methyl-2-pentanone, which is relatively nonvolatile, appears to be lower than expected. The most likely explanation is that it adsorbs on the walls of the sample container and is thus not in the sample presented to the ETHA. If it is in the sample, then it probably adsorbs on the transfer lines. This possibility can be tested by repeating the analysis with the transfer lines at a higher temperature. The pentanone also demonstrates another useful interpretive tool. It has responses in both the positive and negative modes (Figure 6), and the spectra are distinctly different (Figure 7).

An 11 component mixture gives a more complex chromatogram (Figure 8). As shown, the chromatogram is difficult to interpret, but expanding the *x* axis with a built-in software routine shows that each peak is at least partially resolved. One pair of partially resolved peaks illustrates the advantage of having spectral data. *o*-Xylene elutes just before 2-butoxyethanol and gives a much smaller peak; presumably the response factor for the oxygenated compound is larger. Expanding the chromatogram to display elution times between 1950 sec and 2600 sec shows the peaks clearly (Figure 9). The cursor is placed on the baseline just before the elution time of *o*-xylene. The positive mode spectrum in the lower half of the figure is typical of the chromatographic baseline. Moving the cursor to the *o*-xylene peak changes the spectrum to that of *o*-xylene (Figure 10). Moving the cursor into the 2-butoxyethanol peak causes the spectrum to change unmistakably (Figure 11). Not only does the monomer peak shift but a dimer peak appears at a much longer drift time (ca. 7.2 ms).

In this particular example, the peaks of the two compounds happen to be of the same amplitude. If one compound were present at a much lower concentration, the chromatographic peaks may no longer be resolved. The mobility spectrum of the lesser compound, however, could still appear, albeit weaker and for a shorter time. Thus, both target compounds might be detected even though the chromatogram showed only one peak.

A mixture of all 18 compounds tested so far shows a chromatogram in which 16 compounds can be positively identified (Figure 12). Benzene, as mentioned above, has yet to be seen at the low concentration required for toxicological assessments. *t*-Butanol elutes near 2-propanol and *n*-butanol and has a similar spectrum. Identification may be assured by an exact measurement of its elution time relative to the internal standard.

Finally, the total hydrocarbon analysis feature of the ETHA has been exercised briefly (Figure 13). Three sequential exposures to ethyl acetate suggest that reproducibility and the response and recovery times will all be excellent. Like the gas chromatogram, the trace shows the RIP amplitude, which decreases during exposure, and also shows a product ion trace, the monomer (lower trace). The sequence begins on the left of the figure with the first exposure. The RIP amplitude (upper trace) drops almost immediately for 4 of the 5 divisions that constitute full response. Full response is achieved in about 1 *x*-axis division, which is 50 sec. When the ethyl acetate stream is removed, 40% recovery occurs almost at once. After about 100 sec, recovery is over 90%. The monomer peak reaches a plateau almost at once, because it is a steady state intermediate between the RIP and the dimer ion (Figure 2). The short time required for the monomer peak to respond and to begin to recover suggests the IMS cell has a very small effective dead volume. The recovery time is thus probably a function of adsorption in the pneumatics for the THA, which are not heat traced. Two immediate replicate exposures end with the RIP about 1 division lower. This cumulative effect is quite acceptable considering that 5 mg/m^3 is a relatively large concentration that would purge slowly if dead volume or highly adsorptive surfaces were present.

The analytes used here represent a wide range of chemical functionalities. The mobility spectra vary correspondingly and thus the spectra play a major role in data interpretation. Because mobility spectra are usually relatively simple, they have suffered by comparison to complex spectra, such as mass spectra. These ETHA results, however, suggest the value of mobility spectra may have been underestimated. Furthermore, the spectral data are completely independent from the gas chromatographic retention data. This may make them more useful than retention time on a second GC column. As spectral databases become available (Eiceman and Stone, 1995, and Jurs and Wessel, 1995) the ability to identify compounds from their spectra is likely to increase. Finally, peak deconvolution routines such as those used to resolve product ion peaks with similar drift times (Pilon, *et al.*, 1995) might be used to identify trace quantities of one compound in the GC peak of another compound with a different spectrum. In summary, the technique of GC/IMS may be unexpectedly powerful for the analysis of complex mixtures.

CONCLUSIONS

These "first-look" results suggest the ETHA is sensitive and selective for targeted analyses at concentrations found in spacecraft atmospheres. This validates many design choices that led to the chosen hardware configuration and analytical protocol. Another potential problem, peak broadening during injection, does not occur. Precision can only be estimated roughly now, but the constant size of the pinacolone internal standard peak suggests the precision will be acceptable. Response and recovery times in both GC/IMS and total hydrocarbon analysis is excellent. Programming methods and analyzing data with the ETHA software program are very easy. In conclusion, the ETHA appears to be a well balanced, well integrated instrument suitable for further explorations of the potential of GC/IMS and total hydrocarbon analysis.

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5. Pilon, P., Ng, L.K., Mungham, T., and Lawrence, A. 1995. Digital Signal Processing-Use of New and Combined Techniques for the Analysis of IMS Signals, in these Proceedings.

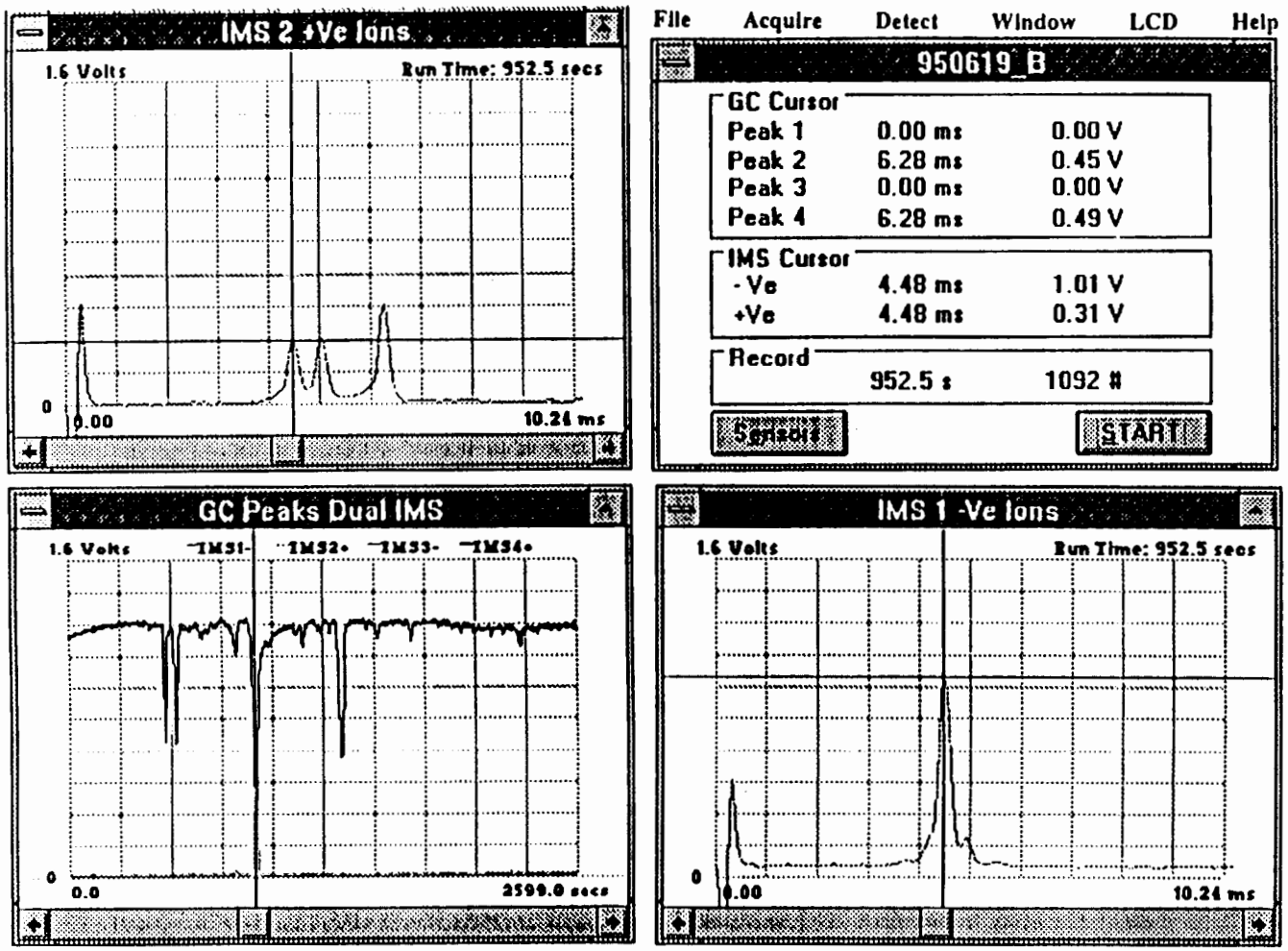


Figure 1. Data output from the ETHA

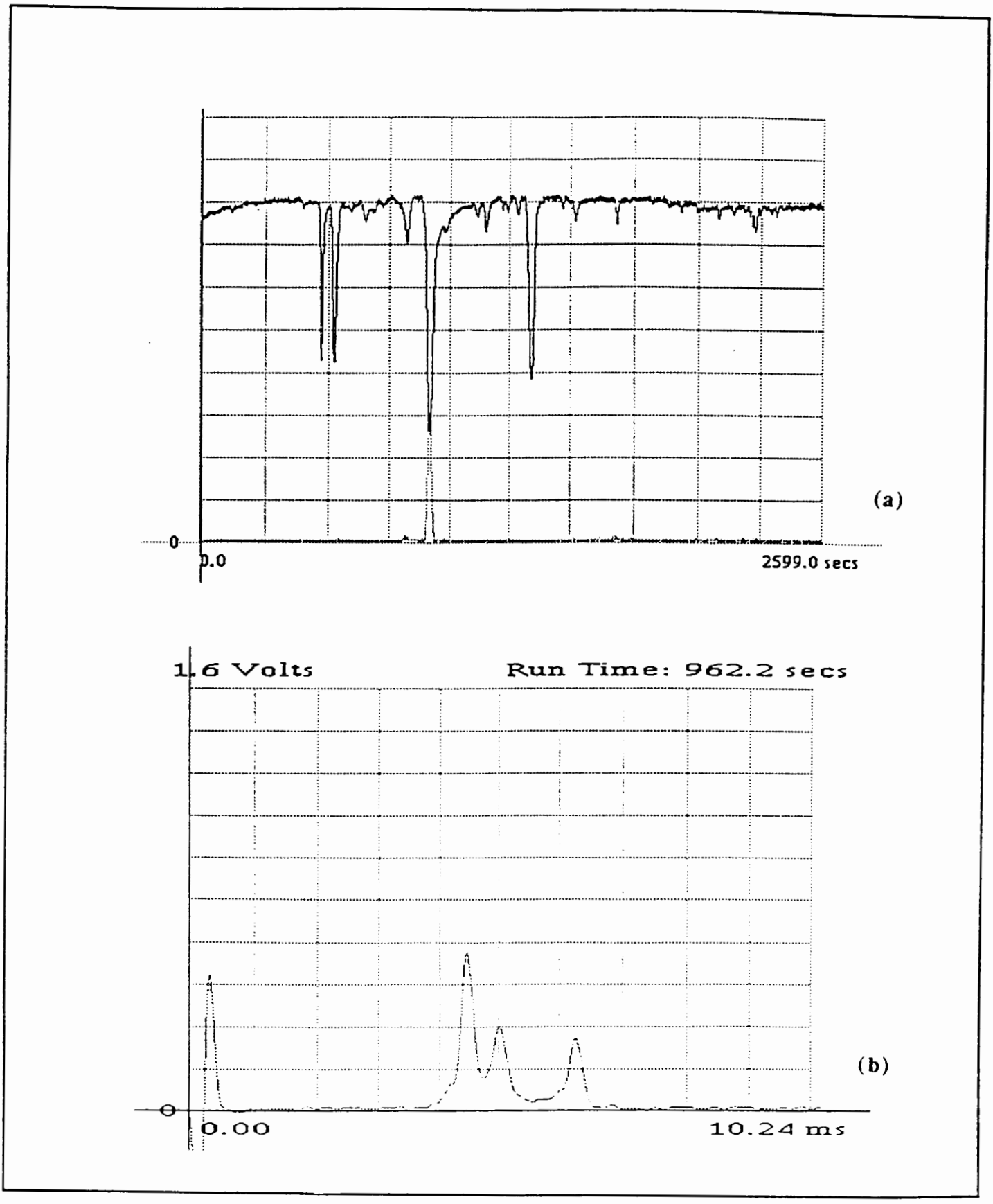
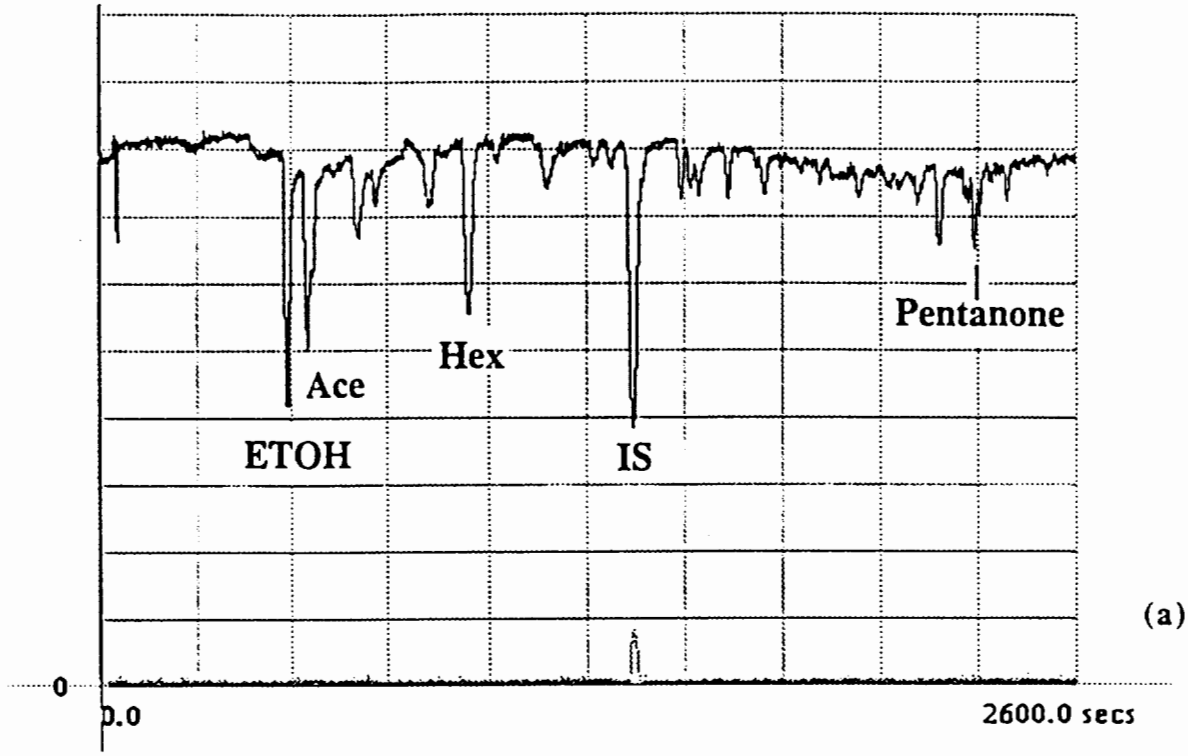


Figure 2. GC/IMS of 5 mg/m^3 ethyl acetate: (a) positive mode GC traces; (b) ethyl acetate positive mode spectrum.



(a)

Ethanol	5 mg/m^3
Acetone	1
Hexane	5
Benzene	0.1
Pinacalone	(IS)
4-Hydroxy-4-methyl-2-pentanone	1

(b)

Figure 3. GC/IMS of a 5 component mixture: (a) positive mode GC traces; (b) components of the mixture.

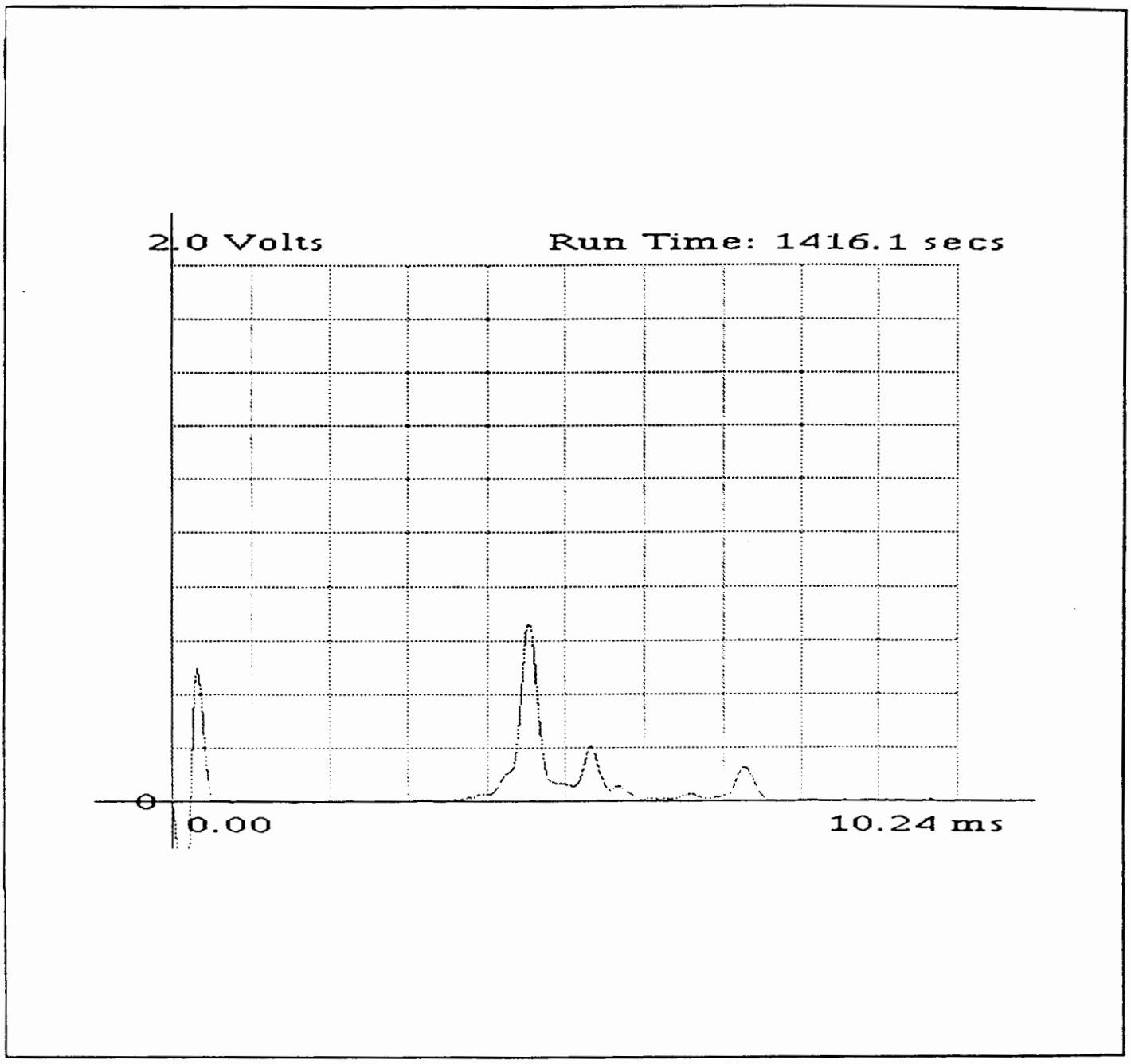


Figure 4. GC/IMS of a 5 component mixture: positive mode IMS spectrum of pinacolone.

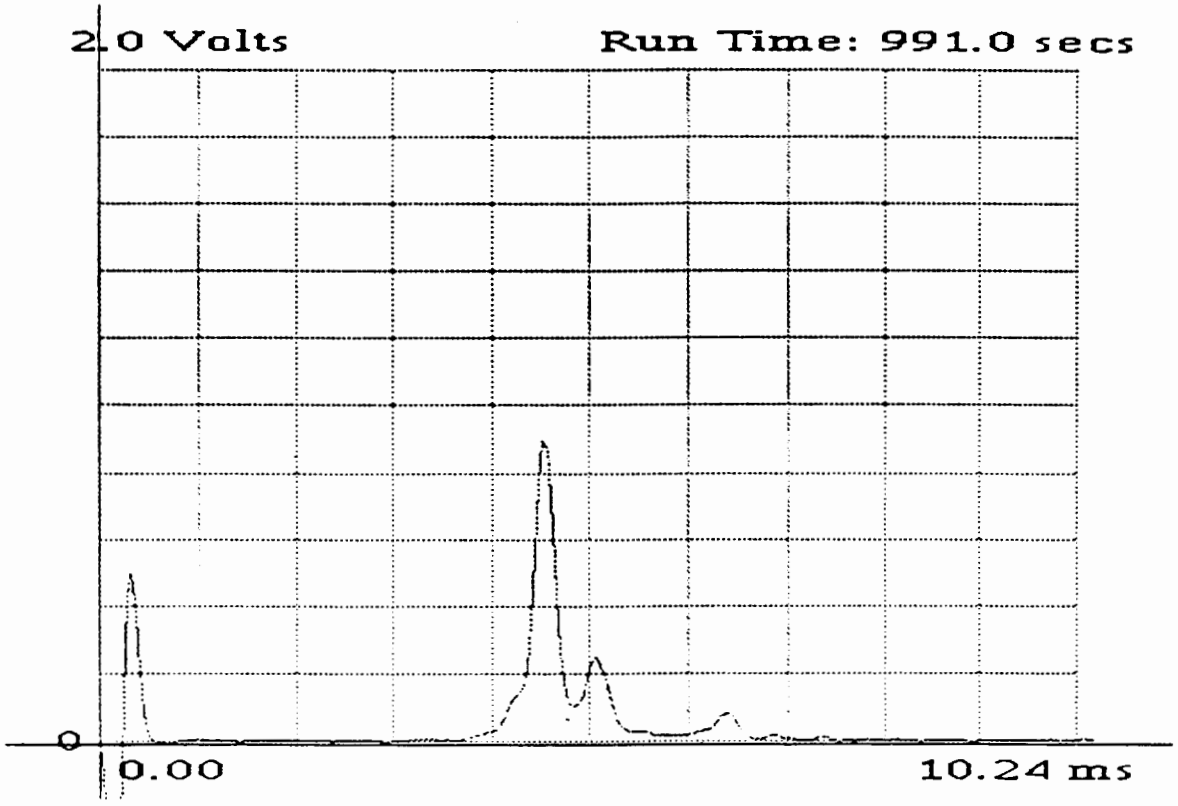


Figure 5. GC/IMS of a 5 component mixture: positive mode IMS spectrum of hexane.

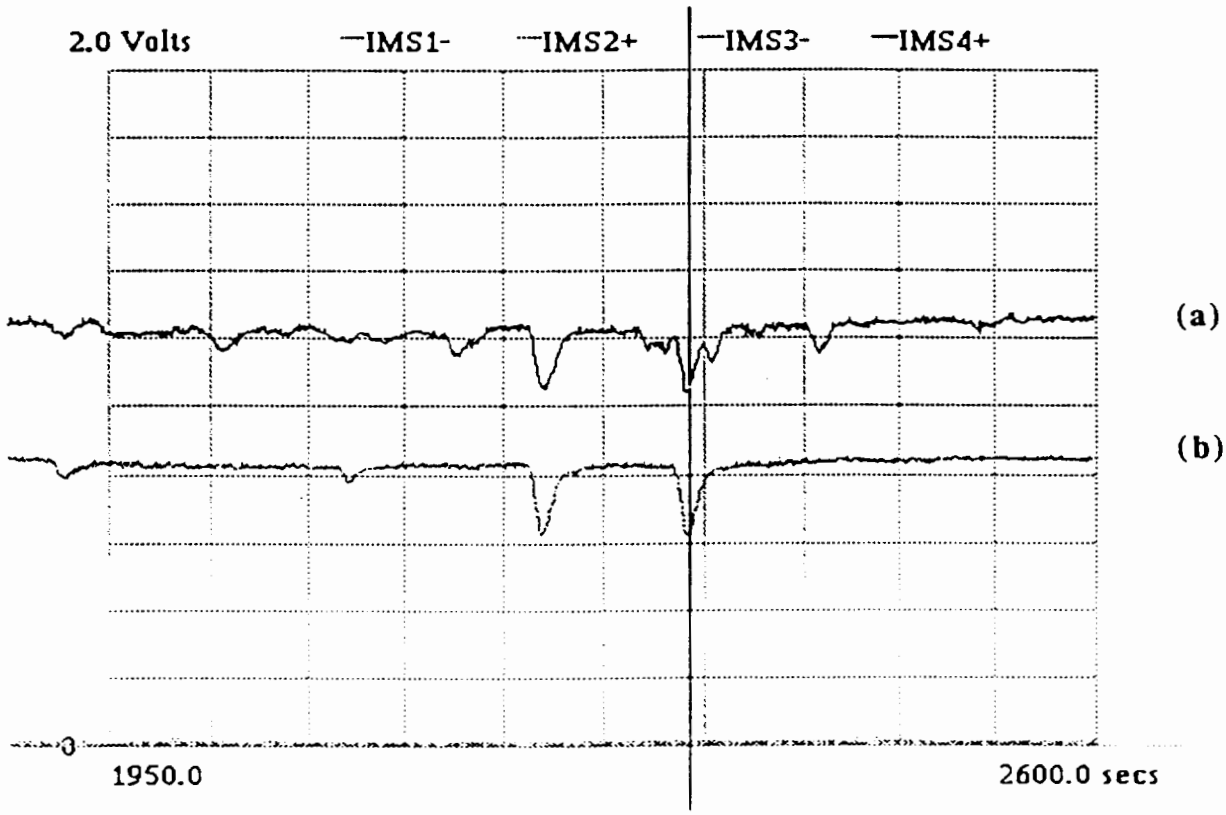


Figure 6. GC/IMS of a 5 component mixture: (a) detail of positive mode chromatogram of 4-hydroxy-4-methyl-2-methyl-2-pentanone elution; (b) negative mode.

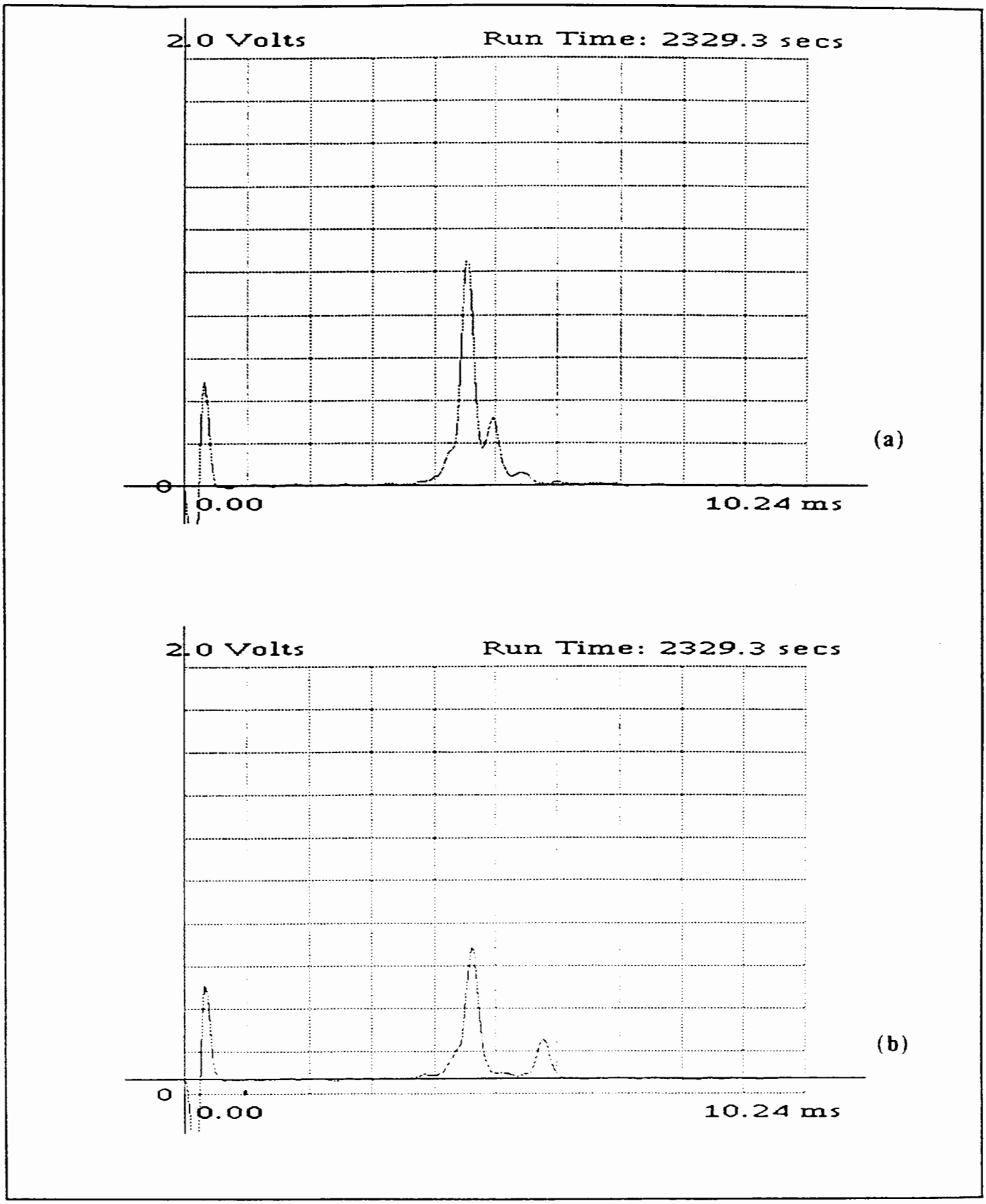
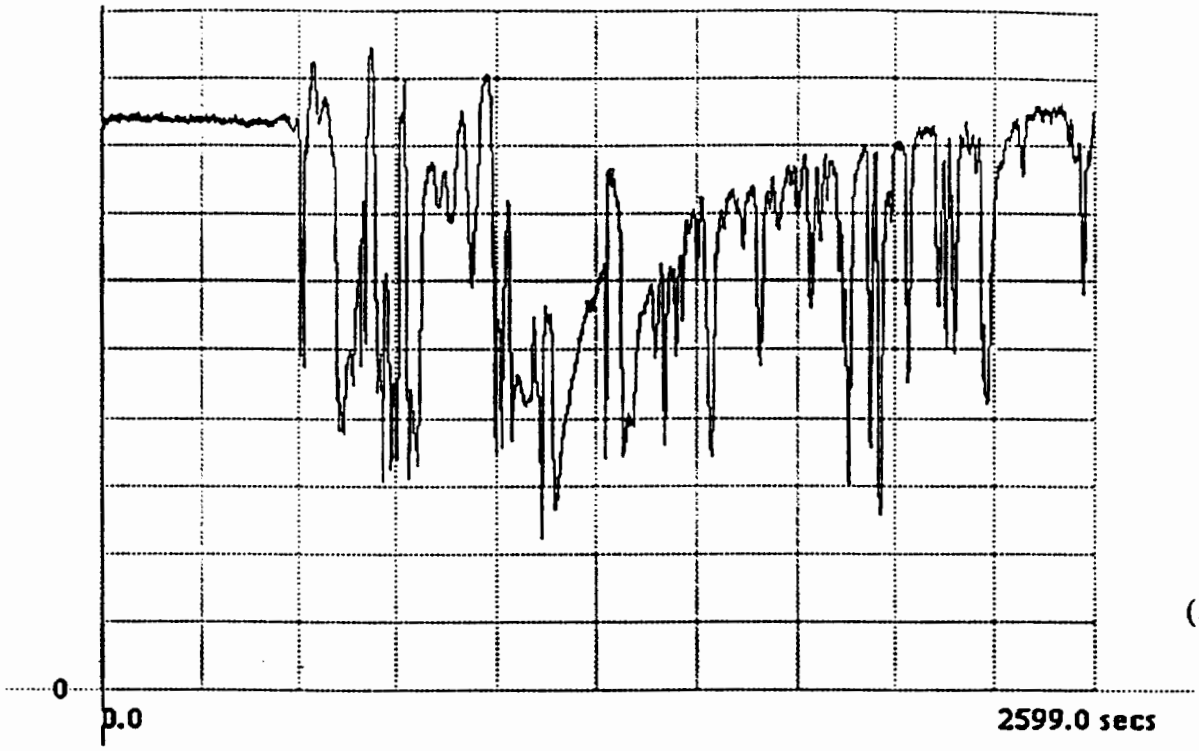


Figure 7. GC/IMS of a 5 component mixture: (a) positive mode IMS spectrum of 4-hydroxy-4-methyl-2-pentanone; (b) negative mode.



(a)

Acetaldehyde	0.5
Methanol	0.5 mg/m3
Isopropanol	5
t-Butanol	5
Ethyl acetate	5
Toluene	3
Xylenes (o, m, p)	10
Hexamethylcyclotrisiloxane	10
2-Butoxyethanol	1

(b)

Figure 8. GC/IMS of an 11 component mixture: (a) positive mode GC trace; (b) components of the mixture.

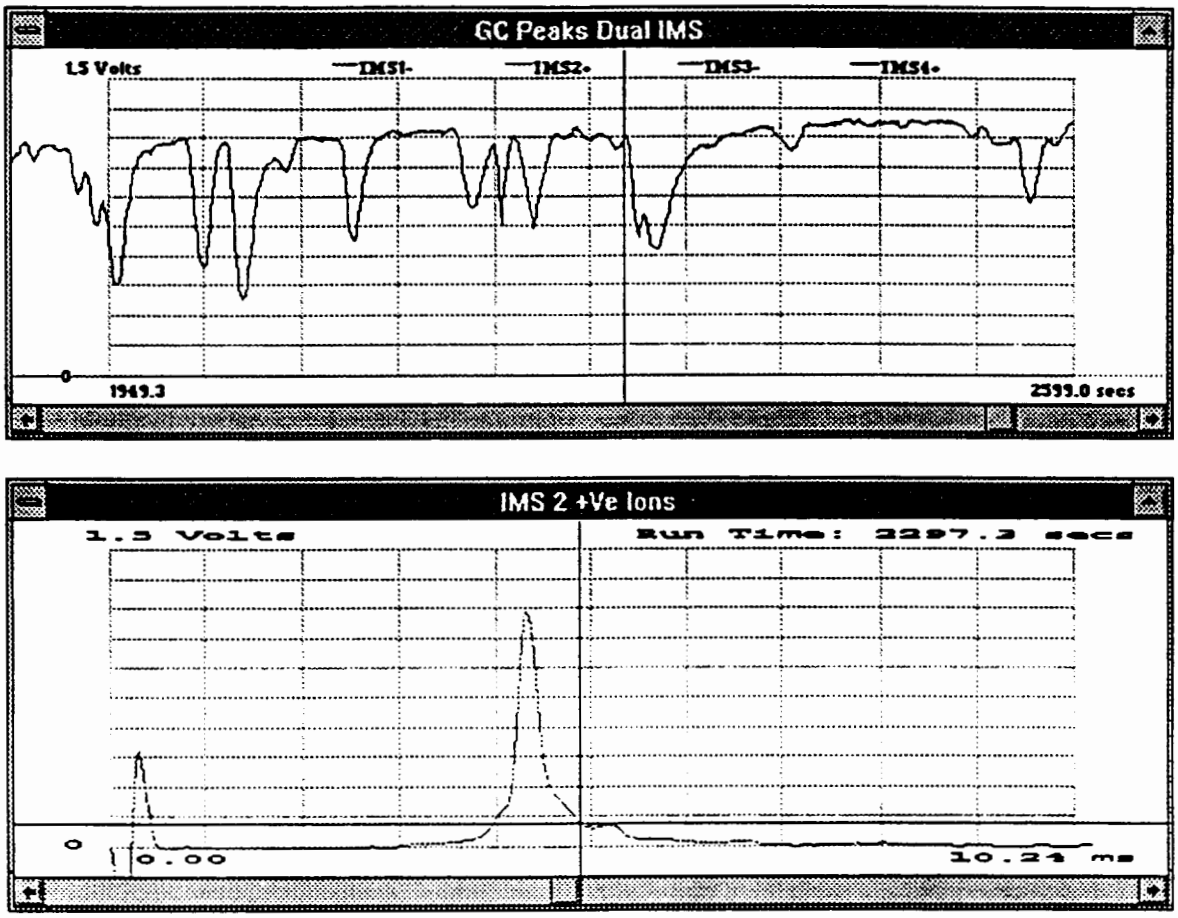


Figure 9. GC/IMS of 11 component mixture: (a) detail showing elution of *o*-xylene and 2-butoxyethanol - cursor is positioned just before elution of *o*-xylene; (b) positive mode IMS spectrum of GC baseline - cursor is positioned on *o*-xylene product ion drift time.

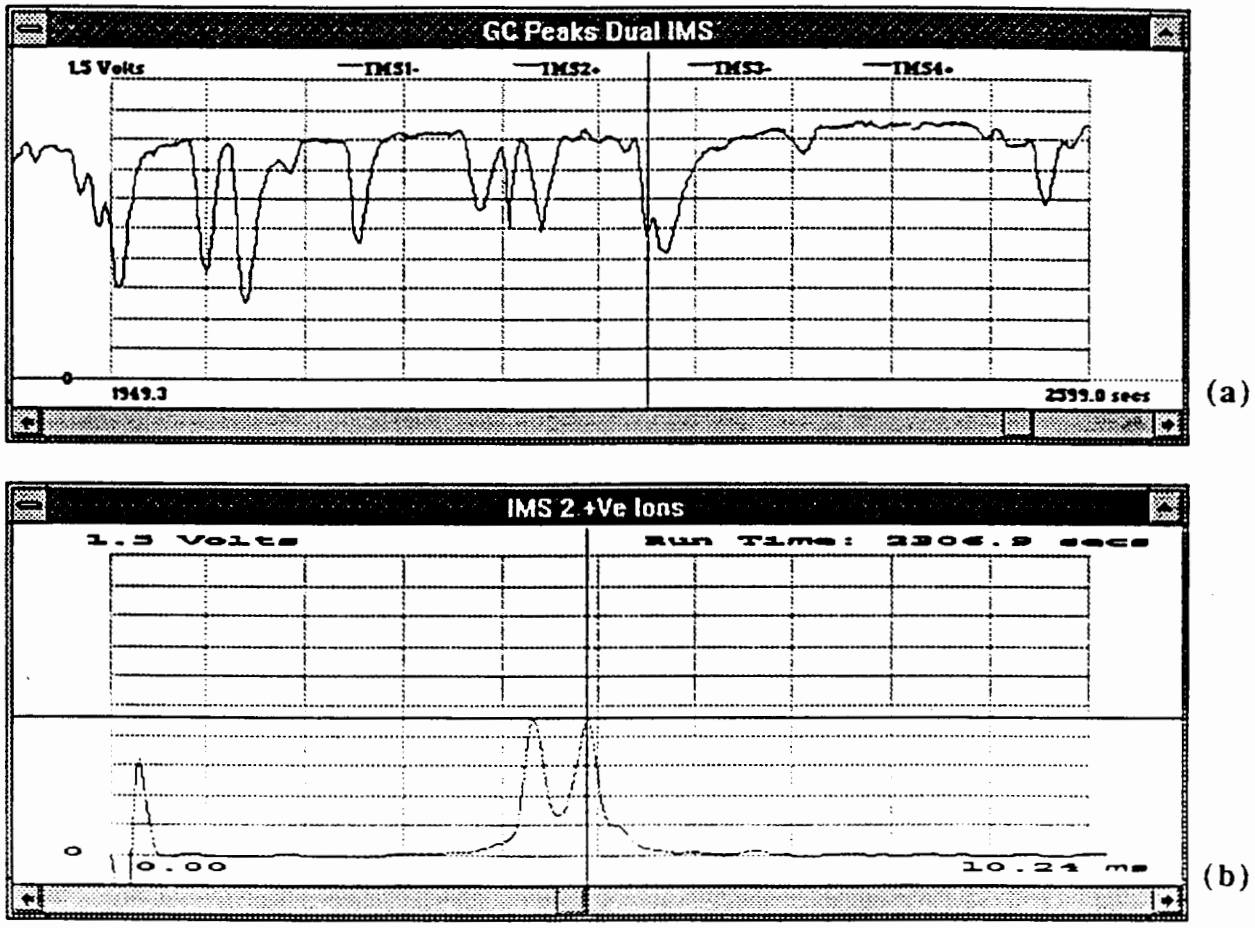


Figure 10. GC/IMS of 11 component mixture: (a) detail showing elution of *o*-xylene and 2-butoxyethanol - cursor is positioned on *o*-xylene peak; (b) positive mode spectrum of xylene.

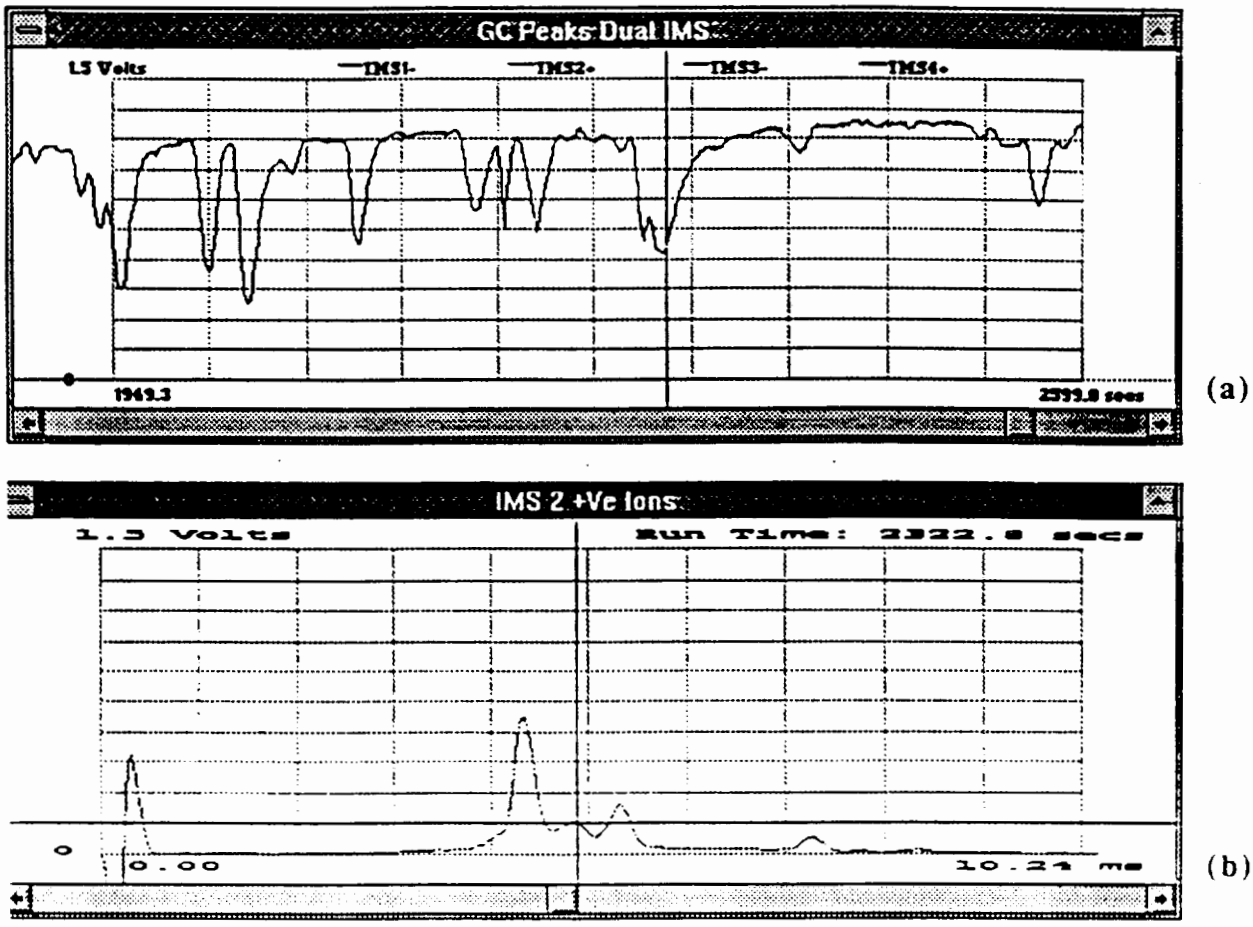


Figure 11. GC/IMS of 11 component mixture: (a) detail showing elution of *o*-xylene and 2-butoxyethanol - cursor is positioned on 2-butoxyethanol peak; (b) positive mode spectrum of 2-butoxyethanol with small concentration of *o*-xylene.

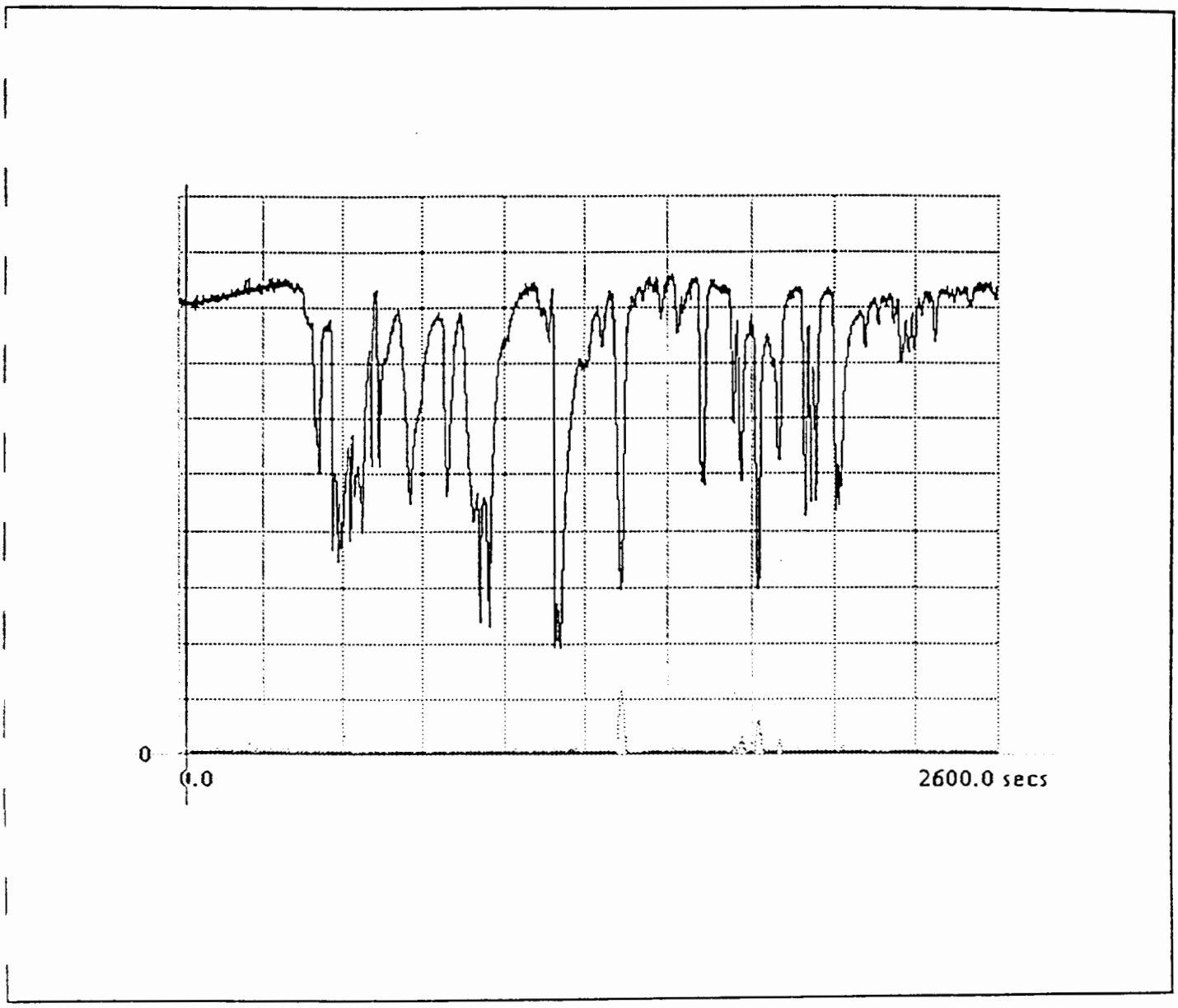


Figure 12. GC trace of an 18 component mixture (positive mode).

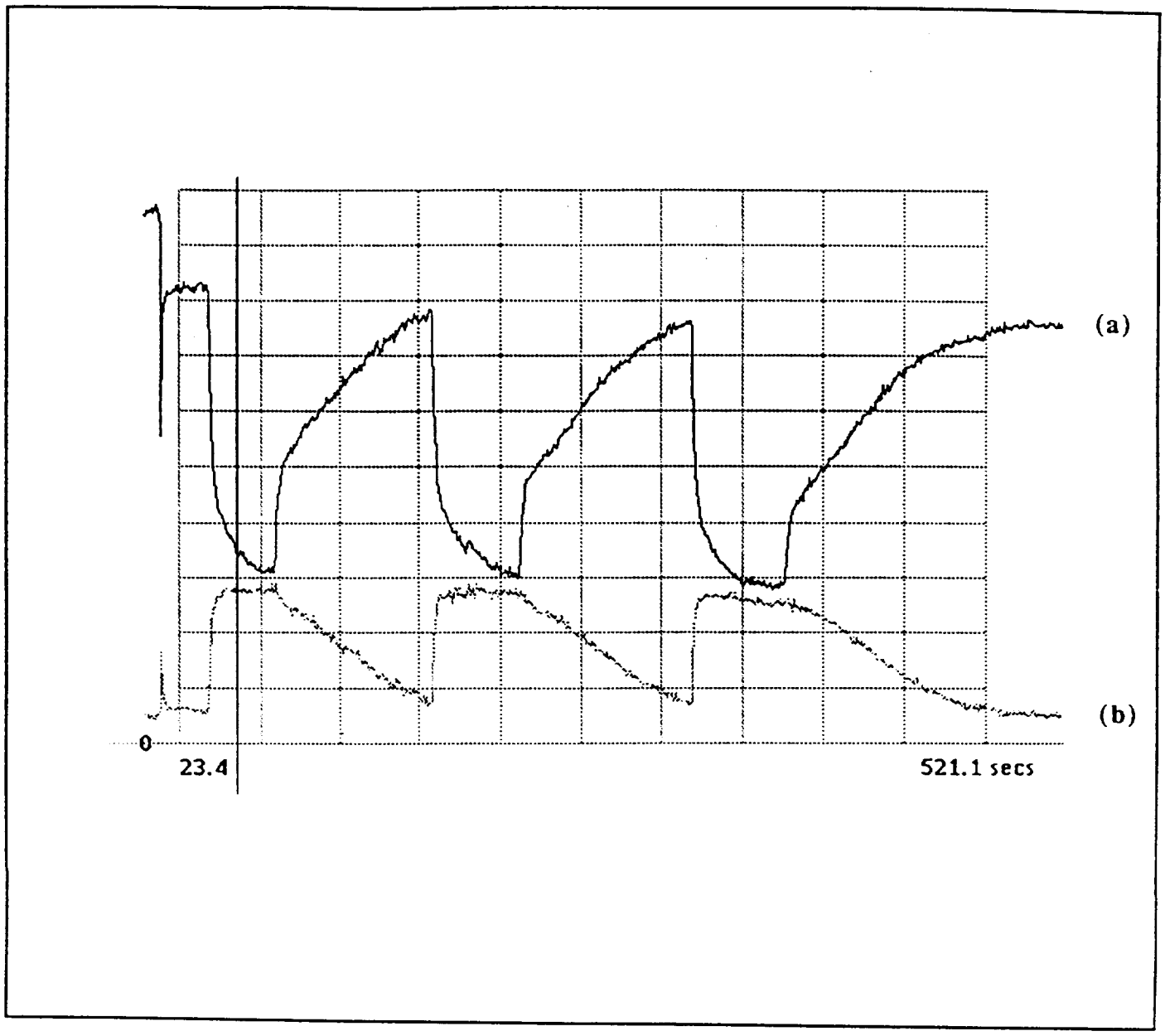


Figure 13. Total hydrocarbon analysis (THA) with 5 mg/m^3 ethyl acetate:
(a) RIP; (b) monomer peak.