Application of time array detection to capillary column gas chromatography/conventional time-of-flight mass spectrometry

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CONCLUSION

TOF-SIMS spectra of PFPE fluids reveal extensive information about the molecular weight distribution and structure of the oligomers. In addition, size-exclusion chromatography of PFPE fluids may be influenced by factors (other than molecular weight) such as the degree of hydrogen-endcapping which produces a change in the tertiary structure of the PFPE and, hence, a change in its molecular volume. Therefore, care should be exercised in the interpretation of SEC data based on molecular weight alone, particularly, for PFPE fluids.

ACKNOWLEDGMENT

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Application of Time Array Detection to Capillary Column Gas Chromatography/Conventional Time-of-Flight Mass Spectrometry

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The technique of time array detection (TAD) is designed to take advantage of the high spectral generation rate available in time-of-flight (TOF) mass spectrometry. In TAD, a number of successive TOF arrival time transient signals are summed to produce each recorded mass spectrum. The TOF/TAD technique offers significant improvements over conventional scanning mass spectrometers for the analysis of capillary GC effluents. Up to 20 mass spectra per second were generated to demonstrate the accurate reconstruction of the chromatographic profile and the lack of mass spectral distortion despite the rapidly changing analyte concentration. Varying the number of TOF transients per recorded spectrum allows the chromatography to be optimized for speed of analysis without sacrificing chromatographic resolution or detection limits. Components of charcoal lighter fluid were chromatographically separated in less than 4 min with quality mass spectra obtained for each eluent.

A major research objective of this laboratory involves the utility of time-of-flight mass spectrometry (TOFMS) for applications where the rate of change of analyte concentration in the ion source is greater than can be accommodated by conventional mass spectrometers (*1*, *2*). A prime example of such an application is high-resolution capillary-column GC/MS. Conventional TOFMS detection schemes involve the use of a boxcar integrator which collects the intensity in only one time window (2–20 ns wide) from each ion arrival time transient (approximately 80 μs long). By collection of the intensity in different time windows for successive transients by this process, the entire mass spectrum can be compiled. The impetus for pursuing TOFMS is the recognition that each arrival time transient (intensity vs time signal) contains data over the entire mass range and that these can be generated at a very high rate (up to 10 000 per second). Detection limits and dynamic range can then be improved by summing successive transients to generate stored mass spectra (scan files) at the rate required for an analysis by high-performance GC/MS. The achievement of maximum GC/MS performance requires the collection of the maximum amount of data available from the sample, in other words, the collection of all information in each ion arrival-time transient and the generation of those transients at their maximum rate (e.g., 10 000 Hz). For this purpose, an integrating transient recorder (ITR) has been built and implemented in this laboratory (*3*). The ITR sums a series of consecutive transients and stores the resulting spectrum to a disk while the next series of transients is being summed. This use of an ITR in TOFMS has been designated time array detection (TAD) (*1*, *2*). As in normal GC/MS, each stored spectrum is called a "scan file" even though, strictly speaking, the TOF/TAD instrument does not scan.

Problems associated with inadequate sampling frequencies when using scanning instruments can be avoided by operating in the selected ion monitoring (SIM) mode in which ion current at only one (or a few) preselected m/z values is monitored. Sampling rate for the selected m/z values is thus increased at the expense of information about the ion currents

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at all other m/z values. Normal TOFMS employs boxcar integration in which the intensity for only a single time window is collected for each transient. In the SIM mode, the time window monitored remains constant. In time array detection, the mass spectral information for all arrival times in every transient is integrated by the ITR. This provides, for all mass values, the same information as conventional TOFMS instruments in SIM mode. Thus, detection limits for complete spectra obtained by TOF/TAD should be the same as those achievable in normal TOFMS only by SIM.

In the application of time array detection to GC/MS, it is necessary that the mass spectrometer achieve temporal focusing at the detector for ions of all masses within the mass range of interest. Unless some method of focusing is used, energy variations of the ions in the source prevent the attainment of unit mass resolution over the mass range appropriate for GC/MS. The well-proven technique of time-lag focusing (*4*), used in early designs of dual source time-of-flight mass spectrometry, corrects for these energy variations by transforming them into a correctable spatial distribution. However, this is a mass-dependent technique, which makes it unsuitable for time array detection over large mass ranges. An additional problem with time-lag focusing is the mass-dependent loss in peak intensities for low-mass ions when the time lag is adjusted to focus high-mass ions.

Limits on the usable m/z ranges for a specified value of time lag have been defined by mathematically correlating intensity and the parameters for unit-mass resolution (*5*). For each value of time lag, the criterion for the acceptable mass range was that none of the nominally equal-intensity peaks was less than 90% of the one with maximum intensity and that all spectra show a separation of adjacent peaks such that the valley between them measured less than 10% of the peak maximum. For example, a time-lag setting that produced an optimum focus at m/z 71, provided acceptable resolution and abundance for ions in the range from 50 to 120 daltons. At another setting, a 100–300 dalton range was suitable for TAD.

This laboratory also has investigated several means of achieving uniform focus across the entire mass spectrum such as with the techniques of beam deflection (*5*, *6*) and dynamic field focusing (*7*). In this report, however, the technique of compromise settings of the conventional time-lag focusing is used (*8*).

EXPERIMENTAL SECTION

Gas Chromatography. A Hewlett-Packard 5790 gas chromatograph was directly interfaced to the mass spectrometer and used in the split injection mode. A 50-m length of 0.25 μm i.d. fused silica column coated with 0.25-mm SE-54 was used for the separations. Column temperature programming was optimized to obtain the desired information in the minimum time. Work based on flame ionization detection was performed by using a Hewlett-Packard 5890 gas chromatograph with a 22-m length of 0.25 mm i.d. fused silica column coated with 0.25-mm SE-54 under similar chromatographic conditions. Helium carrier gas flow rates for all chromatographic tests were adjusted to 1.5 mL/min.

Chemicals. The charcoal lighter fluid was manufactured by Gulf Petroleum, Inc., and purchased in a local grocery store. The gasoline was purchased from a local Shell Oil Co. "service" station. The *n*-decane and toluene were purchased from Fisher Scientific. All products were analyzed as purchased without further purification.

Mass Spectrometer. The instrument used for this work was a CVC 2000 time-of-flight mass spectrometer equipped with a 2-m linear flight tube. The standard detector in the CVC 2000 was replaced with a Galileo FTD-2003 channelplate electron multiplier. Output from the channelplate was amplified by a Comlinear Corp. E220 preamplifier prior to being processed by the ITR. The pulsing circuitry in the CVC 2000 was modified to permit synchronization of the instrument and the ITR. The instrument was focused at m/z 71 (time lag = 0.9 μs), which provides adequate focusing for a mass range of 50–120 daltons.

Integrating Transient Recorder. The ITR was designed and constructed at Michigan State University. As the ITR has been reported elsewhere (*1–3*), it will be described only briefly here. Signals from the mass spectrometer are sampled every 5 ns by a LeCroy TR8828B 200 MHz analog to digital converter, dividing the spectrum into 16 000 5-ns time windows. This permits collection of the entire mass spectrum with sufficient separation of the 20-ns-wide mass spectral peaks. High speed emitter coupled logic circuitry is used to sum and store between 10 and 30 000 successive transient mass spectra into one of two memory banks to collect each spectrum. Simultaneously, the other bank passes the spectrum composed of the previous summed transients to a scan file on the disk. When the first bank has finished collecting a spectrum, the roles of these two banks are switched, ensuring that all data generated are collected.

Microprocessors are used to handle the data transfer from the collection and memory circuitry to a Priam SD107 300-Mbyte hard disk, and the operator interaction with the ITR. The step that currently limits the rate of scan file generation is the process of writing to the disk. By transferring only data from the pertinent mass range to the disk, it is possible to minimize the time spent writing to the disk and to increase the scan file generation rate. Transferring information from 5000 time windows to the disk is adequate to cover a mass range from 50 to 120 daltons and allows a scan file production rate of up to 25 summed spectra per second. Through the use of peak-finding algorithms running in parallel processors, the quantity of data written to the disk can be reduced, a feature which increases the maximum scan file generation rate to more than 60 summed spectra per second. Such a parallel processing system has been installed and software is being written to ensure its full utility. The operator has control over the number of transients summed and, therefore, the scan file generation rate.

RESULTS AND DISCUSSION

Mass Spectral Representation. Qualitative information in GC/MS analyses is gained from the mass spectra. It is therefore necessary to ensure that the quality of the mass spectrum is preserved during data collection. Two features of data collection can influence this quality. The first involves ion counting statistics, while the second occurs from changes in analyte concentrations in the source during acquisition of the mass spectrum.

In a normal scanning mass spectrometer, the intensities of different ion currents are sampled at significantly different times. If the sample concentration in the source changes significantly on the time scale of one mass scan, as in the case when the analyte elutes from a chromatographic column, the mass spectrum will be distorted. This distortion is called "skew" in the spectrum, since it often weights the peak intensities at one end or the other of the mass scale. In the TOF/TAD instrument, the mass spectrum is derived from the population of ions in the source upon application of ion extraction potentials. The nature and amount of ions in the source are functions of the instantaneous concentrations of molecules in the source which vary on the time scale of individual chromatographic peaks. Ion formation is made to occur in a short period of time, up to a few microseconds of the operational duty cycle of the TOFMS instrument (0.1 ms). During the interval of ion formation, ions are somewhat confined by the potential well formed by the electron beam (*9*). The ion concentrations in the source, upon the initiation of ion extraction, are therefore the "leaky" integration of all ions formed during the ion formation process. Since the time required to form and extract ions from the source is at most a few microseconds, analyte concentrations do not change perceptibly. Hence, each transient signal from individual source extraction pulses represents an unskewed mass spectrum. The spectrum contained in each scan file produced by the ITR is a linear sum of these unskewed transient spectra. Thus, the relative intensities at m/z values collected by the TAD process from any point on a chromatographic elution profile are identical within the limits of noise. This is illus-

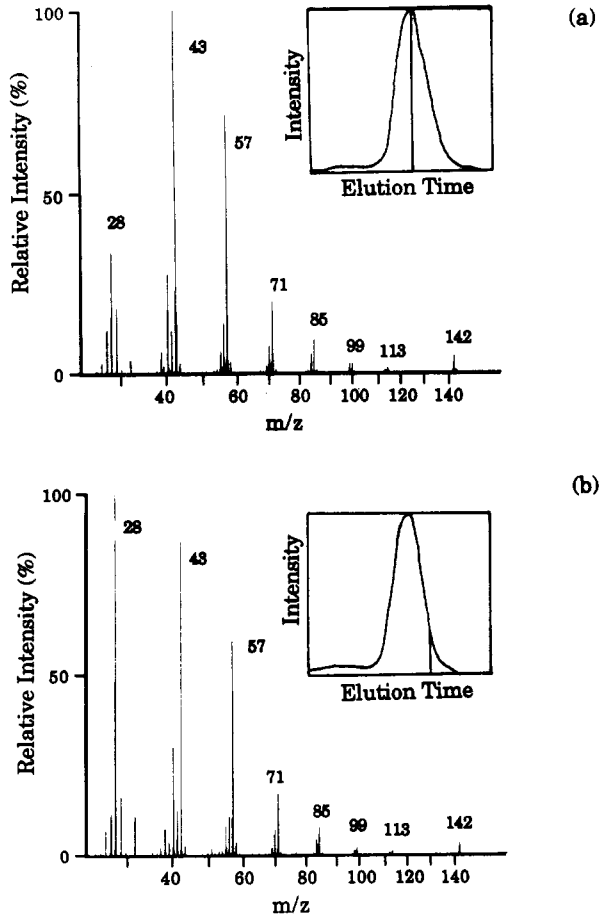

Figure 1. Mass spectrum of *n*-decane collected (a) at the top of the chromatographic elution profile and (b) on the side of the elution profile. The inset in each figure shows the chromatographic profile; a vertical line represents the position on each profile from which the mass spectrum was obtained.

trated by data in Figure 1 in which the spectrum of *n*-decane is shown as acquired at the apex (Figure 1a) and at the side of the elution profile (Figure 1b) at a scan file generation rate of 10 files per second (1000 summed transients per scan file). An air background can be observed in these figures at m/z 28 and 32. Except for this air contaminant, relative mass spectral intensities in these two figures agree within ±3%. Much of the error can be attributed to the background interference in the spectrum collected on the side of the elution profile, which becomes more significant as the partial pressure of *n*-decane decreases in the ion source.

The consistency of relative peak intensities in consecutively recorded mass spectra was assessed under conditions of dynamic partial pressure of *n*-decane as well as under conditions of constant sample pressure. The ratios of peak intensities at m/z 29, 71, and 142 relative to that at m/z 43 were determined in each of 14 consecutive summed spectra (1000 transients summed per spectrum) collected across the chromatographic elution profile of *n*-decane. The ratio of these peaks also was determined in each of 14 consecutive summed spectra obtained from *n*-decane at a constant source pressure. These ratios are presented in Table I. Intensity ratios were consistent within less than 10% relative standard deviation. Smaller values of relative standard deviation were observed for intensities collected under conditions of constant sample pressure than from the chromatographic eluent. This is a result of decreased values of signal-to-noise ratio (S/N) as the partial pressure of *n*-decane is very low at the beginning and end of the elution profile when the sample is introduced through the chromatographic inlet. Mean relative intensities

Table I. Ion Intensities Relative to the Base Peak (m/z 43) for Successive Mass Spectral Scan Files of *n*-Decane under Constant and Dynamic Conditions of Partial Pressure

	reservoir inlet (constant)			chromatographic inlet		
scan	m/z 29	m/z 71	m/z 142	m/z 29	m/z 71	m/z 142
1	18.61	19.62	5.15	19.53	20.71	5.74
2	17.83	20.47	5.62	17.92	20.37	5.88
3	18.60	21.40	5.06	17.53	19.30	5.30
4	18.76	19.19	5.14	19.07	21.86	5.71
5	18.88	19.65	4.57	19.12	20.42	5.27
6	17.56	19.01	5.13	18.56	18.67	5.12
7	17.03	21.58	4.94	19.86	19.38	5.19
8	17.65	20.18	4.98	20.03	18.17	5.31
9	19.21	21.33	4.80	18.19	19.59	4.67
10	18.25	19.46	5.44	17.88	17.48	5.88
11	18.29	19.96	5.29	18.26	19.58	4.49
12	18.85	19.74	5.22	17.81	18.42	5.22
13	20.03	20.41	5.14	17.48	20.86	5.84
14	20.06	21.47	5.43	18.30	20.31	5.55
mean	18.54	20.25	5.14	18.54	19.65	5.36
% RSD	4.7	4.4	5.3	4.6	6.1	8.0

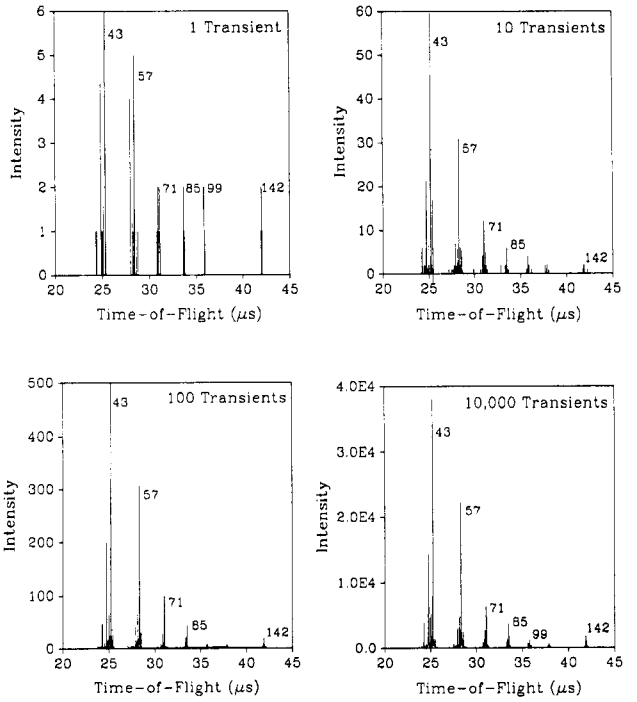

Figure 2. Mass spectrum of *n*-decane collected by summing (a) 1, (b) 10, (c) 100, and (d) 10 000 transient spectra. This corresponds to scan file generation frequencies of 10 000, 1000, 100, and 1 Hz, respectively.

from these two tests were within 1% of each other. This confirms the reproducibility and consistency of spectra acquired under both steady-state and dynamic conditions.

Spectra in Figure 2 were obtained by summing different numbers of transients while the pressure of *n*-decane in the source was held at 5×10^{-6} Torr. These spectra illustrate the improvement in precision obtained by summing additional successive transients. A situation was created where relatively few ions are present in each transient; hence quantization noise is apparent in the spectrum from a single transient (Figure 2a). At very low analyte concentrations, a signal at a given m/z value may be missing in any given individual transient. For example, in Figure 2a peaks at m/z 29, 53, 99, and 127 are more intense than they should be on average, while peaks at m/z 32, 83, 84, and 98 are missing entirely from this spectrum, obtained in 1/10000 of a second. With as few as

10 transients summed (Figure 2b), the spectrum is noisy and not all relative intensities are completely consistent with those in the reference spectrum, but all peaks in the reference spectrum are present. This spectrum corresponds to a scan file generation rate of 1000 Hz. With 100 transients summed (Figure 2c), features of the spectrum are not significantly altered, but a clean, accurate spectrum with a good signal-to-noise ratio is obtained. As large numbers of transients are summed, as shown in Figure 2d, the unprocessed data file exhibits a greater signal-to-noise ratio (S/N) and reveals the Gaussian nature of the peak shapes for the various ion currents.

The improvement in S/N should be proportional to the square root of the number of transients summed as long as the noise is random. A quantitative measure of the S/N was performed by evaluating 50 consecutively recorded summed spectra of *n*-decane consisting of different numbers of summed transients. The reproducibility of signal intensity was determined at several values of m/z. Noise was determined as the variance in the signal intensity. While the value of S/N increases significantly with the number of transients summed per scan file, it does not follow the predicted square root relationship. This nonideality stems from the fact that the prototype version of the ITR produces a nonrandom noise component in the signal that is synchronized to the sampling of the analog-to-digital converter. This component of noise, like the signal, is enhanced with summing. At low numbers of summed transients, white noise (random) is the major contributor to noise in the signal. As the number of transients summed is increased, the random contribution increases as a factor of the square root of the number of transients summed while the synchronous contribution increases in proportion to the number of transients summed. When 2000 or more transients are summed, the synchronous component becomes the major source of noise in the data and the S/N becomes constant. Hence, summing more than 2000 transients with the present version of the ITR does not provide any advantage in S/N.

When both array and scanning systems are limited by white noise or shot noise of the same magnitude, and data are collected over the same range and at the same spectral generation frequency, a multiplex (Fellget's) advantage is obtained by array detection systems over scanning systems (*10*). The multiplex advantage states that an increase in the S/N proportional to the square root of the number of resolution elements is observed for array detectors relative to that obtained by scanning detectors as a consequence of the fact that in the array system, all resolution elements are being continuously monitored. Array and scanning detection systems using the CVC 2000 TOFMS monitor the same signal from the preamplifier, and hence, the noise is comparable. Assuming that readout noise can be neglected, the 5000 time windows used in TAD to cover a mass range of 50–120 daltons would provide an improvement factor of 71 in S/N over that available from TOFMS instruments which use a boxcar integrator with a 5-ns window to scan the spectrum.

Representation of the Chromatography. Information desired from an analysis by GC/MS is usually centered around the identification of chromatographic eluents. A reconstructed chromatographic profile can be used to locate the best spectrum representing the eluting species. The chromatographic representation also contains some quantitative information about the eluents. Insufficient sampling frequencies result in a distortion of the reconstructed chromatographic profile relative to the true elution profile and, hence, a loss of desired information (*1*). Mathematical evaluation of the chromatographic profile requires that as many as 100 data points be collected for each chromatographic peak (*11*), depending on the degree of accuracy desired.

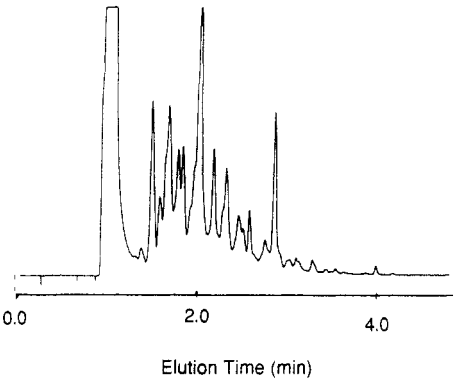

Figure 3. FID chromatogram of charcoal lighter fluid. A 0.5-μL aliquot was injected onto a 22-m length of 0.25 μm i.d. fused silica column coated with 0.25-mm SE-54. The oven was temperature programmed from 100 to 150 °C at 10 °C/min.

The capacity to reproduce accurately the chromatographic profile from a limited number of mass spectra is illustrated in Figures 3 and 4. These figures were collected by using different gas chromatographs under similar chromatographic conditions. The flame-ionization detector chromatogram of a charcoal lighter fluid is shown in Figure 3 and represents the analog chromatogram, unrestricted by the band-pass of the data collection system. The time array detection system permits the selection of effective sampling frequency by providing control over the number of transients summed to create each scan file. The reconstructed chromatograms shown in Figure 4 were obtained from separate analyses of charcoal lighter fluid with different numbers of transients summed per scan file. Differences between Figures 3 and 4 are due in part to the nonspecificity of the flame ionization detector (Figure 3), while the mass spectrometric response may vary from compound to compound. In addition, subtle differences in the chromatographic conditions between the two instruments can alter the chromatographic separation process. The inherent chromatographic peak widths range from 3 to 4 s at base line. The apparent chromatographic resolution increases as the sampling frequency (scan file generation rate) increases from 1 to 5 to 10 Hz (3 to 15 to 30 scan files across the peak profile). Relative chromatographic peak shapes do not significantly change when scan file generation rates above 5 Hz are used. In addition, the signal level in the reconstructed chromatogram decreases as the mass spectral generation frequency is increased, because this causes an associated decrease in the S/N. A scan file generation rate of 5 Hz is thus optimum for these chromatograhic conditions. For different conditions, it is possible to optimize the number of transients summed per scan file to provide the maximum S/N in the mass spectra while maintaining adequate chromatographic resolution.

Serial dilutions of toluene were prepared to determine the detection limit of the TOFMS/TAD system. Quantities of toluene introduced to the mass spectrometer were controlled through injection of aliquots of these standards onto the GC column using a known split ratio and a scan file generation rate of five scans per second. At a signal-to-background ratio of 2, the detection limit was determined to be 3 ng based on measurement of the peak intensity at m/z 91. This is comparable to detection limits found by scanning a quadrupole instrument (Hewlett-Packard 5985A) at its fastest rate.

Speed of Analysis. When the scan rate is not a limiting factor, the chromatography can be optimized for speed, greatly reducing the time needed to perform an analysis. The shorter analysis time results in a corresponding increase in the chromatographic peak heights, compensating for the loss in S/N from the requisite higher scan file generation frequencies.

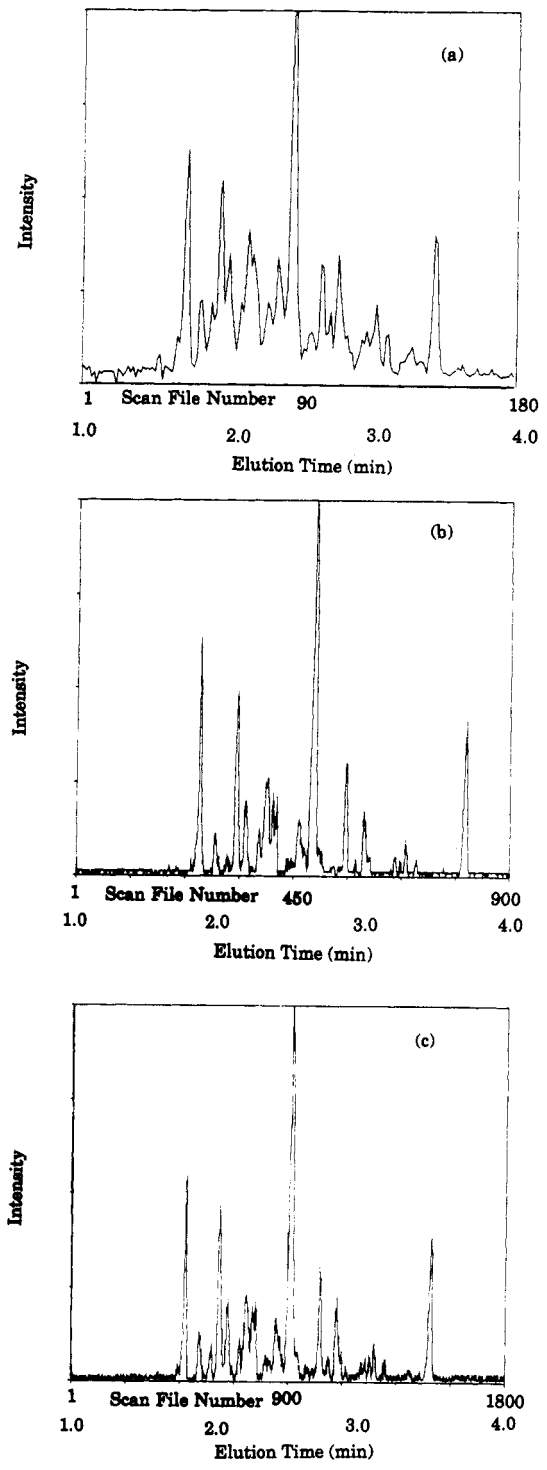

Figure 4. Reconstructed total ion current chromatograms of charcoal lighter fluid from mass spectral databases acquired at scan file generation frequencies of (a) 1, (b) 5, and (c) 10 Hz. The chromatographic time base of all three ion chromatograms is 4 min. Consecutive injections of 0.5-μL aliquots were made onto a 50-m length of 0.25 μm i.d. fused silica column coated with 0.25-mm SE-54. The GC was temperature programmed from 100 to 150 °C at 10 °C/min.

Typical GC/MS analysis times in these cases are on the order of 12–60 min (*12*). The time of analysis can be reduced by altering any of several variables, such as the temperature, column length, or carrier gas flow rate. The reconstructed chromatograms of Figure 4 were generated from data collected during analysis of a charcoal lighter fluid sample in less than 4 min. These reconstructed chromatograms were collected by temperature programming the GC oven from 100 to 150 °C at a rate of 10 °C/min on a 60-m SE-54 column. Chromatograms of gasoline consisting of aliphatic and aromatic hydrocarbons ranging in size up to the trimethylbenzenes have been obtained under similar conditions in less than 2 min. While these conditions are not advisable for the separation of small hydrocarbons, the xylenes and other aromatic isomers are adequately separated. As an example of a more rapid chromatographic elution, the use of a cold trapping inlet with capacitative heating has been reported in the separation of nine of the major components in gasoline in as little as 2.5 s (*13*).

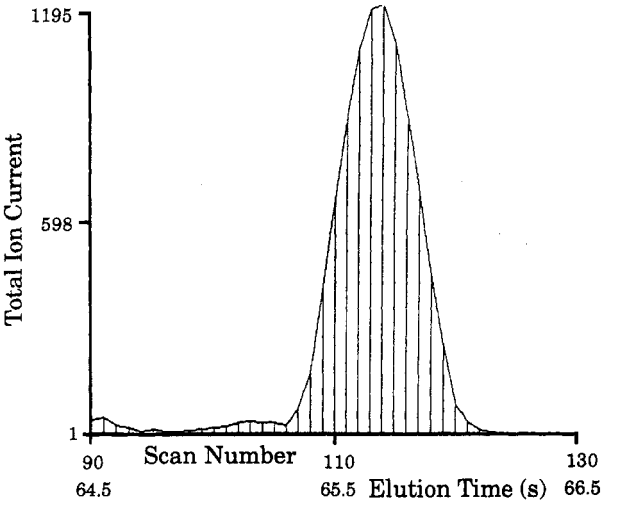

Figure 5. Reconstructed chromatogram of the toluene peak in gasoline. Each vertical bar represents the collection of a summed mass spectrum. A scan file generation frequency of 20 Hz (500 summed transients per scan file) was used to acquire the database.

An example of the scan rate possible with TOFMS/TAD is illustrated in Figure 5, which is a segment of a reconstructed total ion chromatogram representing the analysis of gasoline by capillary column GC/MS. The major peak in Figure 5 represents toluene and corresponds to an injection of about 4 μg into the mass spectrometer source. Scan files used to generate this profile were collected at a rate of 20 spectra per second. Fourteen scan files were collected during the elution of toluene, all of which are readily recognizable as toluene mass spectra. This peak is only 0.7 s wide at base line. The clean peak shape of the reconstructed chromatographic profile shows that peak elution times and areas can be accurately determined at this scan file generation frequency. Without the high sampling frequency offered by TAD, it would have been difficult to collect accurate qualitative and quantitative information for this component by mass spectrometry in a single GC run.

Reducing the time of analysis increases the probability of occurrence of overlapping chromatographic peaks. While this increase is undesirable, many applications exist in which it can be tolerated. Mass spectrometry offers the possibility of deconvoluting overlapping chromatographic peaks when there are unique ions in the spectrum of each component (*14–16*). Inconsistent mass spectra, as well as skewed spectra, complicate deconvolution algorithms by requiring that correction factors or tolerances be considered along with the mass spectral intensities. Because TAD offers the advantage of obtaining unskewed mass spectra across the entire chromatographic elution profile, better success in the application of deconvolution and pattern recognition algorithms can now be expected.

CONCLUSION

The application of time array detection to GC/TOFMS utilizes the full information in each ion source extraction thereby increasing the sensitivity of TOF detection. The

nature of TOF analysis enables mass spectra to be generated in excess of 50 scan files per second. Summation of successive transients increases the signal to noise in the resulting scan file and permits an optimization between the rate of scan file generation (which affects representation of the chromatographic profile) and the quality of the resulting mass spectra. The sampling speed allows complete analysis of each individual ion source extraction and results in accurate fragmentation patterns not affected by changes in partial pressure of the analyte due to the chromatographic process. In the case of overlapping chromatographic peaks, this process yields linear sums of unskewed spectra requiring simpler algorithms for subsequent deconvolution. The combination of high scan file generation rates and simpler deconvolution procedures yields the capacity to reduce the overall analysis time by alteration of the chromatographic parameters. Indeed, it appears that time array detection may be the method of choice for applications of high-speed high-resolution GC/MS.

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Microemulsion Structure and Its Effect on Electrochemical Reactions

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Changes in the microstructure of oil-in-water microemulsions were identified electrochemically by using ferrocene derivatives, methyl viologen, and ferricyanide as the electroactive probes. Microdroplets as well as the bicontinuous microstructure were detected. This was accomplished by determining diffusion coefficients of the probes. Use of probes of different hydrophobicity/hydrophilicity and charge made it possible to investigate different microenvironments of microemulsions including oil, water, and surfactant/cosurfactant interface. Electrochemical reversibility of the probes was affected by the structure and appeared to reflect the ease of mobility across interphases. Reaction potential ($E_{1/2}$) of the probes depended on the composition of the microemulsion.

INTRODUCTION

Microemulsions are of considerable current interest, as model membrane systems, in catalysis and have also been attracting interest in analysis (*1*, *2*).

Microemulsions are three-component solutions that contain water, water immiscible hydrocarbon, and a surfactant. Frequently a cosurfactant, an alcohol, is also present. Microemulsions are thermodynamically stable and macroscopically homogeneous; however, the structure is heterogeneous on a microscopic scale. Interest in microemulsions is due to their solution environment, which combines the properties of hydrocarbons with those of aqueous media and surfactants.

The ordered microenvironment of some microemulsions is also of considerable interest. The microscopic structure of microemulsions depends on composition and is still a subject of debate (*3*). Ordered structures such as microdroplets of oil-in-water (O/W) or water-in-oil (W/O) have been found in microemulsions of high water or high oil content, respectively. The microdroplet structure is similar to the structure of micelles, with the overall larger size of microemulsion droplets. Structures similar to those of normal micelles are present at high water content, and structures like those of reversed micelles are present at low water content (*4*, *5*). So-called bicontinuous structures, with hydrocarbon and water regions stretching over large distances and having no clearly defined structure, have been identified in the intermediate regions (*5*). In this region, as well as in the microdroplets, surfactant and cosurfactant form the oil/water interface (*5*).

Mackay and co-workers have been first to suggest that electrochemical methods can be used to obtain information about the microstructure of microemulsions (*6*). Typically microstructures have been characterized by spectroscopic methods such as light scattering (*7*) and NMR (*8*). Diffusion

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