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The Characterization of Gas Chromatography-
Mass Spectrometry Using Ion Flight Time
and Time-Array Detection

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Eric Douglas Erickson

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THE CHARACTERIZATION OF GAS CHROMATOGRAPHY - MASS SPECTROMETRY USING ION FLIGHT TIME AND TIME-ARRAY DETECTION

By

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ABSTRACT

THE CHARACTERIZATION OF GAS CHROMATOGRAPHY-MASS SPECTROMETRY USING ION FLIGHT TIME AND TIME-ARRAY DETECTION

By

Eric Douglas Erickson

Sample concentrations in capillary gas chromatographic effluent change too rapidly for scanning mass spectrometers to keep pace, which prevents the acquisition of full mass spectral data on each eluting component. A time-array detection scheme has been developed using time-of-flight (TOF) mass spectrometry and an integrating transient recorder (ITR) to increase the sampling frequency of mass spectrometry and overcome this incompatibility. This work describes the application of time-array detection to gas chromatographic effluent, using a conventional, gas-phase TOF mass spectrometer.

Time-array detection involves the monitoring of all ion signals produced by each ion source extraction pulse. Conventional, gas-phase TOF instruments do not provide mass-independent temporal focus, thus limiting the utility of time-array detection. The severity of this mass-dependence has

been examined by means of a computer simulation of factors limiting resolution in TOF mass spectrometry. Windows of usable m/z values have been defined as those with tolerable levels of resolution and intensity degradation. The effect of ion focus parameters on window size and position has been determined. As few as three windows are shown to adequately cover the mass range from 50 to 700 Daltons with a maximum of 10% distortion in relative peak intensity.

Time-array detection schemes were shown to provide several advantages over scanning techniques. The high sampling frequencies possible with the ITR provided the capacity to accurately reproduce a chromatographic profile and avoided problems of mass spectral skew due to changing source concentrations. In addition, enhanced S/N ratios were observed and it was demonstrated that the chromatography could be optimized for speed of analysis. For example, a gasoline analysis can be completed in two minutes.

The high mass spectral scan file generation frequencies that are possible with time-array detection could result in an information overload. A series of algorithms was examined in which the degree of fragmentation of a molecule could be used as the basis for selecting data for the reconstruction of a chromatogram in order to minimize the number of spectra that need to be interpreted. These algorithms were successfully used to discriminate against aliphatic components in the chromatographic effluent and emphasize the aromatic species.

In loving memory of my father,

Commander Douglas Leon Erickson.

ACKNOWLEDGEMENTS

While the work described in this document is the result of my efforts, no major undertaking can occur without the contributions of many others, and this is no exception. I would like to take this opportunity to single out the efforts of other investigators who provided significant contributions and thank them for their tolerance of my idiosyncrasies.

Consultation and moral support have come from everyone that I have encountered in the Chemistry Department at Michigan State University. I would be remiss not to recognize the companionship that I have received from members of the Enke, Watson, and McGuffin groups over the last five years.

Bruce Newcome designed the electronics for the integrating transient recorder and provided assistance in the early days of interfacing this instrument to the time-of-flight instruments. Mike Davenport was always eager to assist me in keeping electronics on both the ITR and the TOFMS operating. Programs on the ITR were written and revised to my demanding specifications first by Russell Rogers and later by Kevin McNitt. These individuals were usually available at all hours to assist in software modifications. Gary Schultz, Mel Micke, Ron Tecklenberg, and Ron Lopshire were always available to serve as an extra pair of eyes or hands, or to act as a critical audience for my many hairbrained schemes. Linda Doherty, Ellen Yurek, Kathleen Kayganich, and Chris Evans were always willing to impart

some of their chromatographic wisdom on me and occasionally even supply me with needed components.

Without the assistance of George Yefchak, the instrument simulation probably would never have reached fruition. Earlier versions of this program were loosely based on one of George's simulations. On later versions, George provided bountiful assistance in program debugging. Thanks to his excellent tutelage and patience, I learned all that I know about programming in FORTRAN and C. Consultations with Stanley Crouch and Tom Atkinson were also very useful in debugging the program.

Funding for this work has come from several sources. Development of the integrating transient recorder and five terms of research support for my efforts was provided through a Biomedical Research Technology Program grant (No. DRR-00480) from the National Institutes of Health. Funding for the MicroVAX computers used for simulations and development of the "degree-of-fragmentation" algorithms was provided in part by a grant from the Office of Naval Research (contract No. N00014-81-K-0834) under the auspices of John Michalski. In addition, I would like to acknowledge receipt of a long term training fellowship from the U.S. Naval Weapons Center, China Lake, California. This fellowship provided support for the first two years of my stay at Michigan State University. In the mean time, the Naval Weapons Center has had to survive without their mass spectrometrist for the last five years.

Finally, I would like to take this opportunity to thank my loving wife, Barbara, and our children, Ivy and Benjamin. Their support and encouragement has made it possible to survive even the toughest of times in graduate school. It has not been easy to return to a life of poverty, but they

have made the best of it. I regret that my research took so much of my time and I hope that I will soon be able to make it up to them.

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OVERVIEW AND PERSPECTIVE

INTRODUCTION

Changes in source concentrations during the elution of species from capillary column gas chromatographic columns occurs on the same time scale as the time required for a scanning mass spectrometer to collect a mass spectrum. This greatly reduces the amount of mass spectral information available for each sample component. An attempt to rectify this situation has been developed based on the use of time-of-flight mass spectrometry (TOFMS) and time-array (TAD) detection [1], which greatly enhances the rate of mass spectral scan file generation. Conventional TOFMS was expected to have serious shortcomings for its application to TAD due to the difficulties in focusing ions of all masses at the detector for every pulse of ions from the source. The principal goal of the research described in this document is to assess the capacity of conventional time-of-flight (TOF) mass spectrometric instrumentation to obtain complete mass spectra of individual components of complex organic mixtures compatible with their elution peak widths from capillary gas chromatographic columns using TAD. This work was performed through an examination of the temporal focusing requirements for ions in conventional TOF instrumentation and an

experimental evaluation of the advantages of time-array detection over time-slice detection strategies.

Complex organic mixtures typically contain large numbers of individual species in widely varying concentrations. Component analysis of such mixtures requires a chromatographic separation to isolate each constituent [2]. Gas chromatography is the most common separation device used for low boiling organic species because of its speed and efficiency. Providing the highest separation efficiency and often the fastest separations, capillary columns have gradually become the separation tool of choice in gas chromatography and are ideal for use in the analysis of complex mixtures [3].

Detection of Gas Chromatographic Effluent

Various detection techniques have been used with chromatographic separations to increase the information content of the analytical process. These techniques include both selective and non-selective detectors. Identification of individual species using a non-selective detector is based on the retention time (or index) of the eluting compounds and the stationary phase used in the separation [4,5,6,7]. These data can be used to obtain chemical information about structurally similar components of the mixture when advance knowledge of the mixture's composition is available [8,9]. A major advantage of non-selective detectors, such as flame ionization [10,11] and thermal conductivity detectors [12], is the ability to detect all components in the mixture, however, little additional information about eluting species is obtained.

Selective detectors are used to differentiate among the many eluting species based on a desired chemical characteristic. Selective detectors such

as the nitrogen-phosphorous [13] or electron capture detectors [14] provide little response to eluents that do not exhibit the particular characteristics sensed by the detector. For example, the nitrogen-phosphorous detector has high response factors for organic amines and phosphonates but has relatively low response factors for (and thus discriminates against) normal alkanes. Mass spectrometers can be used as selective detectors by using selected ion monitoring (SIM). This approach involves setting the mass filter to pass only ions of a single m/z value which is characteristic of the class of compounds to be detected [15]. This added degree of selectivity provides more information concerning the detected compounds, but distinctions among detected species are still restricted largely to the regime of chromatographic retention time. This technique increases sensitivity to a single molecular structure at the expense of information about all other components.

The ideal universal detector would respond to all eluents but in a manner that is distinctive for all possible components, thereby ensuring that all components are detected and eliminating the reliance of identification on retention indices. This requires the simultaneous detection of diverse qualities of eluting species, hence the use of multichannel detectors. Multichannel detectors that have been used for such purposes include several spectroscopic [16,17] and mass spectrometric [18] detectors, with the latter being more predominant as a gas chromatographic detector in analytical labs. These detectors provide a distinct spectrum for most eluting species, providing non-specificity by responding to most eluents and increased specificity in the spectral domain at the same time. Both optical and mass spectrometric detectors can offer many channels of structural information. While many electronic transitions are available for optical detection, practical transitions are often limited by available wavelengths of impingent radiation.

Mass spectrometers rely on the ability to remove (or add) electrons to the analyte and hence are slightly more universal detectors than are spectroscopic detectors. Both techniques use similar detection strategies, so sensitivity in these detectors is largely a function of the cross section of the analyte to photons or electrons. The capability of these types of detectors to provide multiple channels of information and a high degree of sensitivity produces more information intensive data than other chromatographic detectors.

Chromatographic Requirements on Spectral Detectors

Detectors which collect spectra must perform their data collection on a time scale much shorter than that of the chromatographic elution peak. Peak area (first moment) calculations require around 30 to 60 spectra per peak elution profile while higher order moment analyses often require sampling frequencies in excess of 100 spectra per peak [19]. An inadequate sampling frequency can result in serious errors in reconstructed chromatograms. This fact is demonstrated in Figure 1.1, which compares a hypothetical elution profile and reconstructions of it from different numbers of discrete data points. Using a sampling frequency of about 3 samples per peak, the reconstructed chromatogram of Figure 1.1b is obtained. This figure shows an adequate qualitative representation of chromatographic components, but the quantitative information is degraded by significant changes in peak height and area. The situation is even worse for Figure 1.1c where the same sampling frequency was used, but there was a phase-shift in the sampling frequency versus th GLC peak relative to that of Figure 1.1b. Qualitative aspects of the data are affected as well. Increasing the sampling frequency to 5 samples per peak, as in Figure 1.1d provides a more accurate reproduction

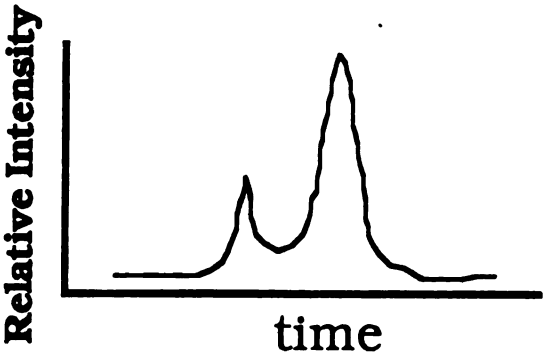

Fig. 1.1a

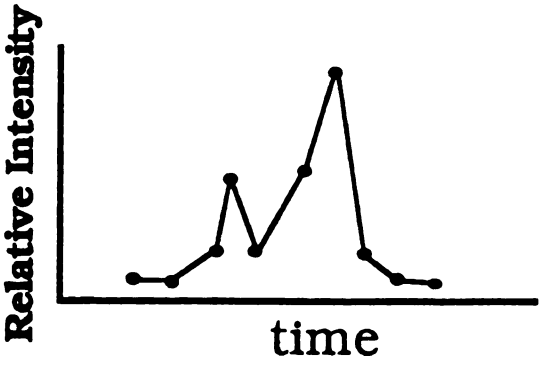

Fig. 1.1b

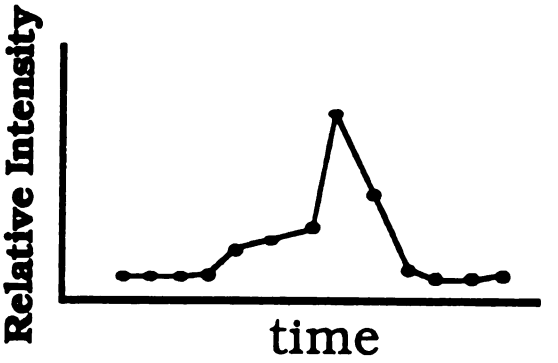

Fig. 1.1c

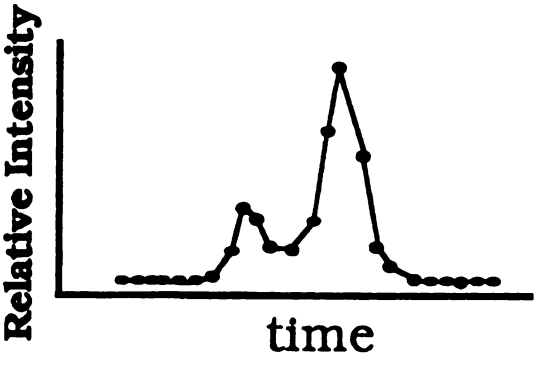

Fig. 1.1d

Figure 1.1. The effect of sampling rate on the reconstruction of chromatographic profiles. (a) A simulated chromatogram. (b) Reconstructed chromatogram from 3 points across the peak. (c) Reconstructed chromatogram from 3 points across the peak, not synchronized to the elution profile. (d) Reconstructed chromatogram from 5 points across the peak.

of the chromatographic profile. Because it is not possible to synchronize chromatographic elution times with data collection times for scanning instruments, it is necessary to use high sampling frequencies to avoid loss of qualitative and quantitative information during the data collection process.

Capillary column chromatographic elution peak widths can now be produced that are on the order of one second. Such high performance chromatography requires sampling frequencies of 30 Hz or higher. It is necessary to sample all avaliable windows of information at this rate. Array detectors permit the simultaneous collection of all windows of information, permitting high data acquisition rates [1]. However, instruments that are presently used to scan a spectrum multiplex the detector among the many windows, reducing the detection time per window by the number of available windows. This process can lead to an additional degradation of the qualitative nature of the data when the scanning time is long relative to the rate of change of sample concentrations, as illustrated in Figure 1.2. Figure 1.2a is a simulated steady-state hypothetical mass spectrum with three peaks of equal intensity. Since spectral intensity is proportional to sample concentration; sampling the hypothetical species over the concentration gradient of Figure 1.2b would result in the skewed spectra of Figures. 1.2c through 1.2e, depending on which portion of the concentration profile was used during the spectral collection interval. This effect increases the difficulty of spectral interpretation when relative intensities of the various windows are involved in the component discrimination process.

Because signals within a window of information are not measured continuously by scanning detectors, much signal is lost resulting in a raising of the detection limits. Lower detection limits can be achieved through the

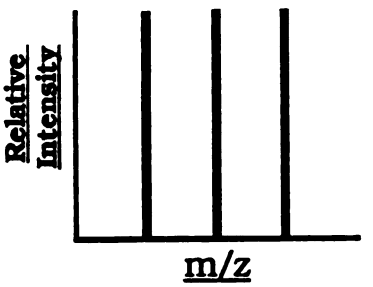

Fig. 1.2a

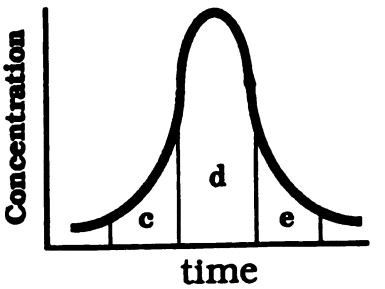

Fig. 1.2b

Fig 1.2c

Fig 1.2d

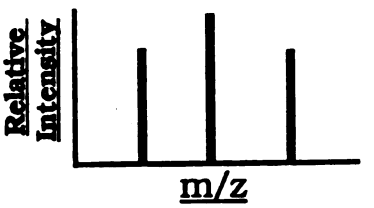

Fig 1.2e

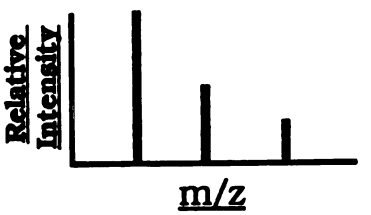

Figure 1.2. The effect of sampling rate on mass spectral quality. (a) A hypothetical mass spectrum collected under ideal conditions. (b) The concentration gradient across which spectra are obtained. (c) The mass spectrum obtained from the rising edge of the concentration profile. (d) The mass spectrum obtained at the top of the concentration profile. (e) The mass spectrum obtained on the falling edge of the concentration profile.

use of a detector which continuously collects information in a channel, as in array or specific detectors. In addition, a multiplex advantage is realized for array detectors over scanning detectors that increases the signal-to-noise ratio by a factor of the square root of the number of contributing elements [20].

Scanning Mass Spectrometric Detectors

The detrimental effects of scanning the spectrum that were described in the previous section only become significant when the detector scan time is significant with respect to the chromatographic elution peak widths. Scanning methods in mass spectrometry typically require 0.5 to 2 seconds per scan to cover the entire mass range and obtain sufficient ion statistics. This spectral generation rate is clearly inadequate for the narrow chromatographic peaks that can be produced using capillary gas chromatographic columns.

A quadrupole-based mass spectrometer has been built for the analysis of systems in which concentrations change rapidly, such as the detection of thermal detonation products [21,22]. This instrument continuously scans the spectrum at a rate of 0.3 ms per Dalton over a 1 to 200 Dalton mass range. This instrument permits the acquisition of a 100 Dalton mass window in 30 ms, which is adequate for the sampling requirements of a gas chromatographic detector. However, it has a limited mass range and poor mass resolution. Additionally, the investigators had difficulty storing the resultant data at the requisite high rate. They ultimately resorted to high speed photography of an oscilloscopic image.

Array Mass Spectrometric Detectors

Array detectors permit the acquisition of spectral data at a much higher frequency than scanning detectors. Several mass spectrometric array detection schemes have been developed that could prove useful for this application.

An electro-optical ion detector has been developed as an array detector for magnetic sector instruments [23,24]. This device takes advantage of the fact that magnetic sector instruments disperse the mass spectrum in the spatial domain. Through the use of a microchannel plate electron multiplier connected to a photoplate and a diode array detector via optical fibers, the spatial distribution of ions at the detector is transformed into an array of m/z values. Problems associated with the use of this type of detector include spreading of peak intensities into adjacent channels limiting both the resolution and dynamic range of the detector, fluctuations in the gain from one channel to the next, and a limited mass range. While recent advances have extended the mass range of this technique [25], there is a trade-off between mass range and resolution or signal quality.

Fourier transform mass spectrometers (FTMS) use the precession of ions in a magnetic field to obtain a spectral array in the frequency domain. This technique has been used to monitor the effluent from capillary gas chromatographic columns [26]. Spectra can be obtained in the time frame of tens to hundreds of ms [27], which is adequate for keeping pace with the chromatography. However, the technique requires that very few ion collisions occur. This limits pressures in the analyzer region to no more than 10^{-8} torr. Such pressures are difficult to maintain when the instrument is interfaced to a gas chromatograph. Other problems with FTMS include a

memory effect, the requirements of uniform magnetic fields in the analyzer cell, and a limited dynamic range because of space charging within the cell.

A third array detection technique for mass spectrometry, and the one used for this study, has been developed based on time-of-flight mass spectrometry (TOFMS) and an integrating transient recorder (ITR) [28,29,30]. The TOFMS transforms the mass spectrum into the time domain by giving all ions nearly equivalent kinetic energies in the direction of the detector. Ions of different masses have different velocities and thus different flight times to the stationary detector. For ions of the same mass to arrive simultaneously requires an ion bunching technique to convert the ion velocity distribution into a distribution of arrival times at the detector. Bunching can be achieved by pulsing the source, deflecting the ion beam, or sinusoidal modulation of the source and the detector [31]. Wiley-McLaren style commercial instruments use a pulsed source with an extraction frequency of 10 KHz [32]. TOF instrumentation has the unique advantage of producing a complete mass spectrum for each extraction pulse from the source [33]. It is, therefore, conceivable that 10,000 complete mass spectra could be collected each second. Hence, TOFMS has the potential to deliver mass spectral sampling frequencies more than high enough to meet the requirements of capillary chromatography. This feature attracted Gohlke to use TOFMS as the first mass spectrometric detector for gas chromatography [34]. Unfortunately though, his data collection system was limited to photographic reproductions of a Techtronics oscilloscope. So, while TOFMS offered the requisite high mass spectral generation frequencies, it was limited until recently by data storage techniques. With the development of time-array detection and its ability to rapidly store data to a disk, TOFMS becomes a viable tool for keeping pace with rapid changes in source concentrations

observed when measuring effluent from capillary gas chromatographic columns.

The distribution of ion arrival times that is produced at the detector from a single source extraction pulse is transformed into a transient electrical signal of about 100 μs duration. This transient signal contains all the information necessary to reconstruct the entire mass spectrum. In its conventional time-slice (scanning) detection mode, however, 2 s are required to collect information from the entire mass range. Time-array detection (TAD) uses the integrating transient recorder to sum successive transients and store the resultant summed spectrum to a disk as a scan file, permitting the collection of up to 66 scan files (complete mass spectra) each second. This spectral generation rate is presently high enough to meet the needs of capillary column gas chromatography.

Limitations of Time-of-Flight Mass Spectrometry with Time-Array Detection

Use of the ITR to perform time-array detection permits the collection of information within all discriminating channels of data available by mass spectrometry at a sampling frequency which is adequate for gas chromatography. However, several problems remain with the TOF-TAD system when used for gas-phase analyses. Among the problems are the poor mass resolution of TOFMS when gas-phase sources are used and the massive quantities of data that are generated when high mass spectral collection frequencies are used.

Initial energy, spatial, and velocity vector distributions in the source limit resolution in conventional TOFMS. Velocities of ions leaving the source are a function of their kinetic energy. Most of this kinetic energy is acquired

as the ions pass through the potential fields in the source. However, the total ion kinetic energy is the sum of all sources of kinetic energy, and any initial distribution of ion energies will result in a distribution of ion velocities and hence a distribution in ion arrival times at the detector. This source of error is usually minimized by using high extraction potentials, on the order of 3 kV, which greatly reduces the relative contribution of the thermal energy to the ion's total kinetic energy.

The initial energy dispersion can also be reduced through energy filtering [35] or focusing [36] of ions after they leave the source. Energy filtering will remove all ions that lie outside of a small window of energies while focusing will result in isomass ions of all energies arriving at the detector simultaneously. While these techniques minimize peak spreading from energy dispersion in a mass-independent manner, they do not compensate for other sources of poor mass resolution in TOFMS and may still result in a mass-dependent focus.

The potential field experienced by an ion in an electric field can be compared to a hill, with the top of the hill being the maximum potential obtainable within the field. The amount of energy gained by an ion going down this hill is a function of the starting point on the hill. A distribution in spatial positions in the source results in ions gaining different energies in leaving the source, and thus a distribution in the kinetic energy of the ions. In this manner, the spatial distribution is converted to an energy distribution. The problem gets worse as the extraction potential increases. Any distribution in the kinetic energy of the ions is transformed into a distribution of ion arrival times at the detector. Gas-phase sources have large spatial distributions of molecules in the source region, increasing the

probability that a large dispersion of initial ion positions will occur. The distribution of ions in the source is commonly assumed to be confined to the volume defined by the beam of ionizing electrons [37]. This electron beam passes through a narrow slit, minimizing the thickness of the ion packet in the source region. In 1955, Wiley and McLaren designed a two-stage source which helps compensate for this initial spatial distribution of ions through the creation of a plane at which isomass ions that originate from different positions in the source with the same initial kinetic energy arrive simultaneously. Placing the detector at this space focus plane ensures optimal focus of ions with initial spatial distributions.

The final source phenomenon that affects resolution is the initial distribution of ion velocity vectors. Ions with velocity vectors pointed away from the detector acquire the same kinetic energy in the source as do ions headed towards the detector, but they must turn around in order to leave the source. The time needed to perform this act , the "turn around time", results in ions leaving the source with the same velocities but at different times. The magnitude of this effect is reduced by increasing the extraction potential. Along with their two-stage source, Wiley and McLaren developed the technique of time-lag focusing in which a delay time between ion formation and ion extraction from the source is used to permit ions to move in the source as a function of their mass and initial velocity. In this manner, the initial velocity distribution is transformed into a spatial distribution which is compensated for by placing the detector at the space-focus plane. This technique permits a mass-dependent correction for the "turn around" effect.

Mass-dependent focus is inconsequential when a single m/z value is monitored for each extraction of ions from the source. In this case, the focus

can be readjusted before each ion extraction pulse for the ion being monitored. However, when using an array detection scheme which monitors all ions produced by each ion extraction pulse from the source, a mass-dependency to the focus is detrimental to the resultant spectrum. No one value of time lag or other focusing parameters will suffice to keep the entire spectrum in focus.

Ion mirrors (reflectrons) [38] can be used to increase the obtainable resolution of TOFMS instrumentation. These instruments permit the acquisition of a complete mass spectrum in 25 μs with no resolution degradation [33]. Therefore, these instruments have the potential to provide the needed resolution for gas chromatographic analyses while still providing high mass spectral scan file generation frequencies. However, reflectrons have the capacity to correct for either the spatial or energy dispersions in the source, but not both [39]. For this reason, they are seldom used for gaseous sources and are used most frequently in applications with planar sources such as ^{252}Cf plasmas [40], molecular beams [41], SIMS [36], and LAMMA [36]. Since gas chromatography requires a non-planar, gas-phase source, the reflectron is not currently appropriate for use in this application.

Attempts to modify conventional TOFMS instrumentation to improve resolution and alleviate the mass-dependency problem have included beam modulation [42,43], energy filtration followed by beam modulation [44], post source pulsed focusing [45], and time-dependent potentials applied to ion acceleration grids [46,47]. Until such a mass-independent means of focusing TOFMS spectra is obtained, it would be useful to identify regions of the spectrum in which acceptable signal quality is obtained for preset mass-dependent focus parameters. In this manner, the focused region of the

spectrum could be changed for successive ion source extraction pulses, with focused regions patched together to obtain the complete spectrum. Chapter 2 of this thesis covers an investigation into this possibility.

The use of the TAD system has several advantages over scanning systems. These include the capability to accurately reproduce the chromatographic elution profile, to obtain unskewed spectra of gas chromatographic eluents, to improve the signal to noise ratio, to optimize the chromatography for speed of analysis, and to collect all the information generated during the analysis. These advantages are discussed in detail in Chapter 3 of this thesis.

With the high chromatographic sampling frequencies possible using array detection methods in conjunction with TOFMS instrumentation, comes a large quantity of data that must be reduced in order to complete the analysis. A half hour gas chromatographic run with a mass spectral scan file generation frequency of 20 Hz produces 36,000 mass spectra. Generally, only a limited number of these spectra are analytically useful. It is therefore necessary to develop a strategy that will rapidly permit the identification of analytically useful spectra with a minimal interaction from the analyst. One such strategy is examined in Chapter 4 based on the degree of fragmentation observed in the mass spectrum.

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CHAPTER 2

MASS DEPENDENCE OF TIME-LAG FOCUSING IN TIME-OF-FLIGHT MASS SPECTROMETRY

INTRODUCTION

Time-array detection uses the signals from all m/z ions produced from each extraction of ions from the TOFMS source. If ion focus at the detector is dependent on mass, resultant spectra will have poorly resolved peaks in regions of the spectrum that are distant from the m/z value that is in focus. Focusing of TOFMS ion packets in conventional, gas-phase instrumentation involves the adjustment of source parameters. Unfortunately, these deviations in source parameters are not mass independent, and conventional instrumentation does not provide the opportunity to further refine the focus after ions leave the source. The work described in this chapter was initiated in order to ascertain the severity of this mass dependence when conventional instruments are used to monitor large regions of the mass spectrum.

ION FOCUSING IN TIME-OF-FLIGHT MASS SPECTROMETRY

Temporal focusing of isomass ions having different initial energies is obtained in conventional time-of-flight mass spectrometry (TOFMS) by means of a delay time (time-lag [1]) between ion formation and extraction from the source and by adjustment of the extraction grid potentials. During

this time-lag, the initial kinetic energy of the ions causes them to be displaced from their incipient positions. Delay times are selected such that ions which at the time of extraction are farthest from the detector catch up to ions whose positions at the extraction time are closest to the detector. Extraction grid potentials are adjusted so that this coincidence occurs at the detector surface. The optimum delay time for the extraction pulse is a function of the mass-to-charge ratio of the ions being focused. Figure 2.1 illustrates the influence of this mass-dependence for the m/z 502 and 503 ions of perfluorotributylamine. With the proper focus, seen in Figure 2.1a, the peaks at m/z 502 and 503 are well resolved. The spectrum in Figure 2.1b was collected with the focus optimized for m/z 28. In Figure 2.1b, the peak at m/z 503 appears as an extension of the shoulder of the 502 peak, reducing the qualitative and quantitative information available in this region of the spectrum.

As discussed in Chapter 1, the mass-dependence of this focusing technique is inconsequential when only one m/z ion is monitored for each extraction pulse, as in time-slice detection [2]. In this case, focus parameters are adjusted for successive extraction pulses and thus the optimum focus is obtained for the m/z ion being monitored. However, this scanning data collection technique results in the loss of information concerning all other ions in the transient mass spectrum because these ions are not being observed [3]. As shown in Chapter 1, it is desirable when monitoring systems in which concentrations are changing rapidly, such as chromatographic effluent, to avoid the loss of chromatographic or mass spectrometric information by using high sampling frequencies. These high sampling frequencies can be achieved using time-array detection [3], but this technique

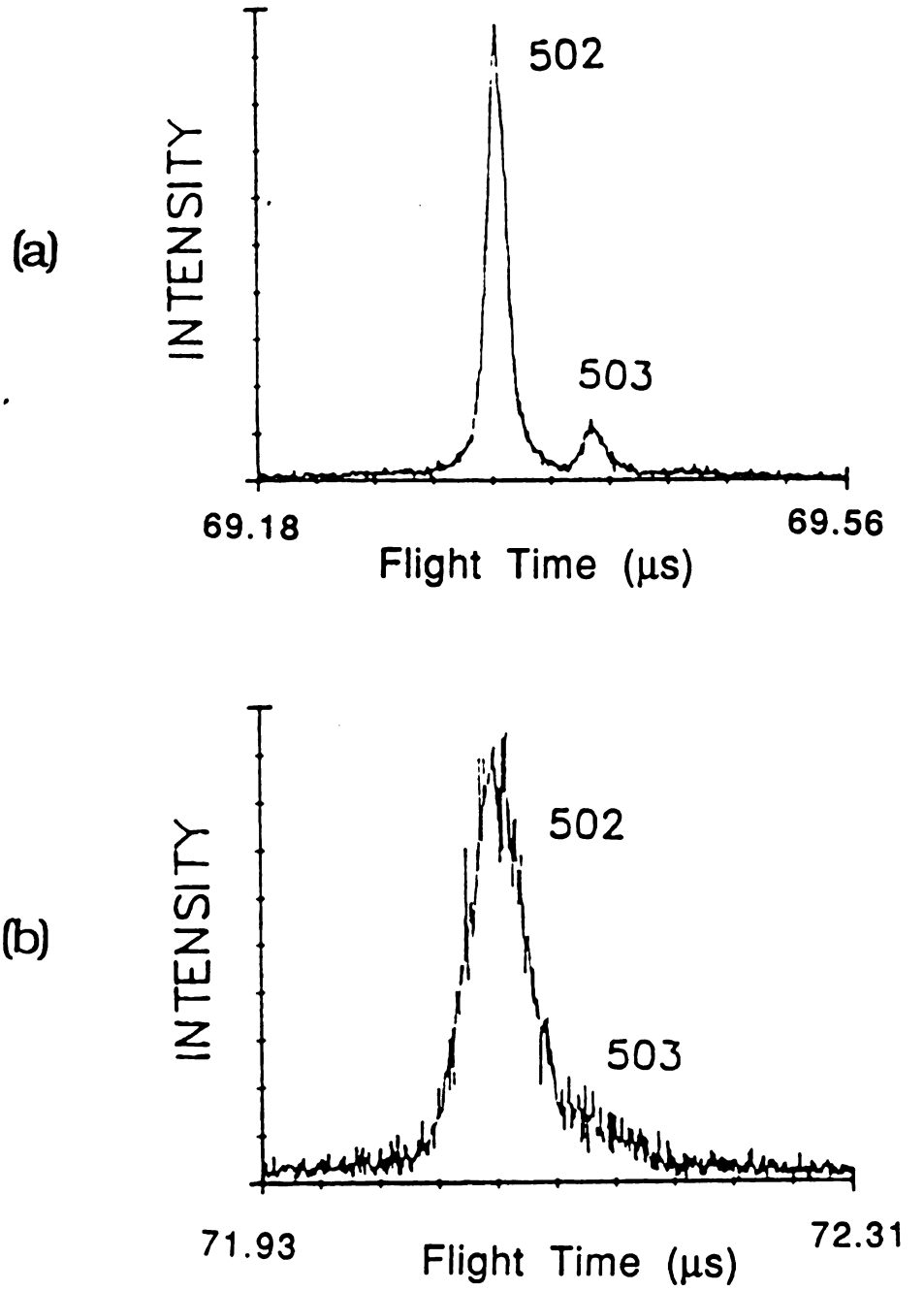

Figure 2.1. The mass-dependence of time-lag focusing in time-of-flight mass spectrometry. Shown are m/z ions 502 and 503 from the spectrum of perfluorotributylamine with the value of time lag optimized for (a) m/z 502 and (b) 28.

requires that a large range of m/z ions be monitored from each extraction pulse, making mass-dependent focusing undesirable.

Several instrumental modifications have been examined in an attempt to eliminate the mass-dependency of ion focus in TOFMS. Among these are beam modulation [4], energy filtering in combination with beam deflection [5], post source pulse focusing [6], and dynamic-field focusing [7]. Each of these approaches requires modification of the TOFMS instrumentation, with the latent complications of additional ion optics and instrument electronics.

The approach taken during this investigation was to investigate the use of conventional instrumentation with a succession of time-lag settings, each providing a mass window of acceptable focusing without prohibitive signal degradation. By using conventional instrumentation over smaller mass windows, TOF-TAD could be put to immediate use while more eloquent solutions to the ion focus problem can be developed. However, this approach requires that the number of sequential time-lag settings used to cover the instrument's mass range be small or the time required to collect full mass spectra will be too long to provide full mass scans at the rates required by high-performance chromatography. Use of a multi-time-lag approach necessitates the capacity to predict the boundaries of such mass windows. This chapter is the result of efforts to determine the severity of the resolution degradation caused by time lag, and to characterize the effects of other instrumental parameters on the temporal focus of ions in a commercial, linear, gas-phase TOFMS, the CVC 2000.

Sources of poor resolution in TOFMS include the initial spatial, energy, and velocity distributions of ions in the source as well as velocity distributions from metastable decompositions after ions leave the source. Due to the difficulty of finding molecules which have fragment ions throughout the mass range of the instrument and which do not undergo metastable decompositions, a computer simulation of the CVC 2000 TOFMS instrument was developed. This simulation permitted the characterization of the instrument and examination of factors that limit performance; studies that would have been difficult or impossible using data generated exclusively from the instrument. When possible, simulated data were compared with experimentally obtained data.

A schematic representation of the source and ion drift regions in the CVC 2000 instrument is presented as Figure 2.2. This instrument has a 4-grid ion source with a 2 m field-free drift tube. Electrons are pulsed into the ionization region of the source for a period of time controlled by the operator. The first extraction grid is held slightly positive with respect to ground while the backing plate is held at ground to provide a confining potential for ions in the source region located a distance s_1 from the exit grid for the first region. The second grid is also held at ground during this time period. While the electron beam is passing through the source, ions are confined to the potential well formed by this electron beam [8]. After the electron beam has been deflected away, the ions' thermal energy causes them to drift within the ionization region. Upon expiration of the time lag, a square wave pulse of magnitude V_1 and ramp time t_r is applied to the first grid to initiate extraction of ions from the source. A second square wave pulse of magnitude

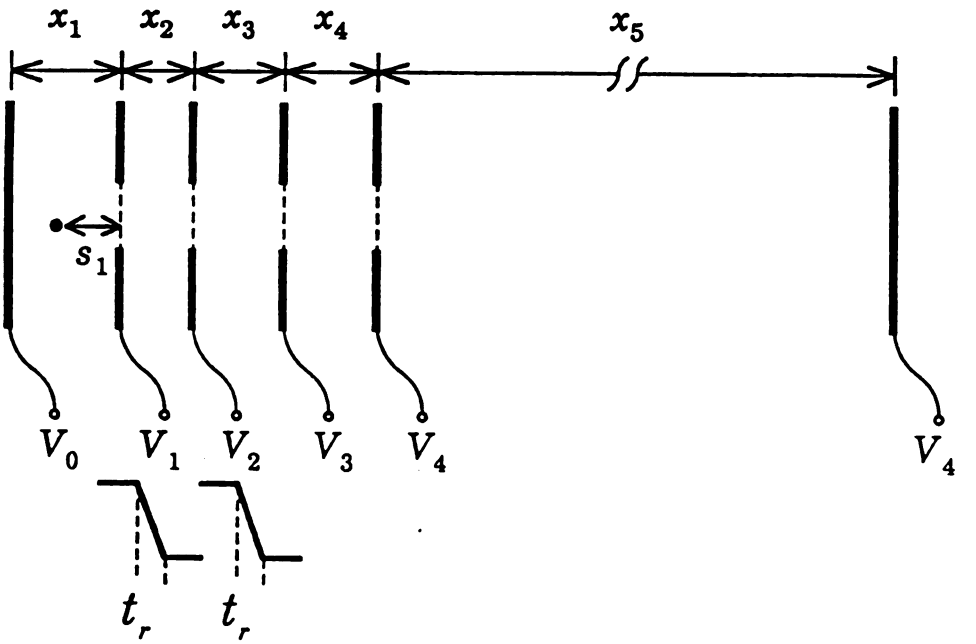

Figure 2.2. A schematic diagram of the CVC 2000 Time-of-Flight Mass Spectrometer. Typical voltages and distances are included in Table 2.1.

V_2 is simultaneously applied to the second grid. Remaining grids in the source are held at steady-state potentials to ensure that ions do not experience changing fields after leaving the source. Instrumental parameters used on the CVC 2000 were measured and are listed in Table 2.1. Values in Table 2.1 were used in simulations of instrument performance. Focus parameters that have been examined as a part of this work include the duration of the time lag, the magnitude of voltages applied to the first two grids, and the ramp time needed to achieve the maximum voltage on the first two grids. Those factors that have been shown to have the largest effect on ion focus are the time lag and the V_1 potential.

Table 2.1. Instrumental Parameters

Parameter	Value
x_1	0.0037 m
x_2	0.0017 m
x_3	0.0061 m
x_4	0.0056 m
x_5	2.1 m
s_1	0.0020 m
V_{1i}	+0.44 V
V_{1f}	-6 to -140 V
V_{2i}	*0.0 V*
V_{2f}	-150 to -250 V
V_3	-1400 V
V_4	-2700 V
t_r	30 ns

Flight time calculation

The acceleration, a, of a charged particle in an electric field is described by Equation 2.1:

$$a = qV / mx \tag{2.1}$$

where q is the charge on the particle, V/x is the potential field experienced by the particle, and m is the particle's mass. The velocity, v, and distance traveled, s, within each region can be calculated through integration of Equation 2.1 with respect to time. The total flight time of an ion is the sum of the flight times through each of the individual regions:

$$t_{of} = t_1 + t_2 + t_3 + t_4 + t_5 \tag{2.2}$$

Each individual flight time can be calculated from the solution of quadratic or cubic equations.

Potentials on the first two grids in the source are pulsed between initial (V_{1i} and V_{2i}) and final (V_{1f} and V_{2f}) voltages as listed in Table 2.1. Since ideal square waves cannot be obtained, it takes a certain time, t_r, to reach the final potential. Hence, the possibility that ions leave a region before t_r has elapsed should be considered. This results in several possible flight times through the first three regions of the source. Table 2.2 contains the equations of motion for ions in each of the 5 regions in this instrument. In the development of these equations, the voltage rise was approximated by a linear ramp between the initial and final voltages applied to grids 1 and 2. Using this approximation, the voltages on these two grids before time t_r is

Table 2.2 Equations of motion for cases where t_r expires while ion is before, after or within each region.

Before Region	After Region
Region 1:	$v_1 = \frac{qt_1^2}{2mx_1t_r}(V_{1f} - V_{1i}) + \frac{qV_{1i}t_1}{mx_1} + v_0$ $s_1 = \frac{qt_1^3}{6mx_1t_r}(V_{1f} - V_{1i}) + \frac{qV_{1i}t_1^2}{2mx_1} + v_0t_1$
Region 2: $v_2 = \frac{qt_2}{mx_2}(V_{2f} - V_{1f}) + v_1$	$v_2 = \frac{qt_2^2}{2mx_2t_r}(V_{2f} - V_{1f} + V_{1i}) - \frac{qV_{1i}t_2}{mx_2} + v_1$
$s_2 = \frac{qt_2^2}{2mx_2}(V_{2f} - V_{1f}) + v_1t = x_2$	$s_2 = \frac{qt_2^3}{6mx_2t_r}(V_{2f} - V_{1f} + V_{1i}) - \frac{qV_{1i}t_2^2}{2mx_2} + v_1t_2 = x_2$
Region 3: $v_3 = \frac{qt_3}{mx_3}(V_3 - V_{2f}) + v_2$	$v_3 = \frac{2V_3t_3}{mx_3} - \frac{qV_{2f}t_3^2}{2mx_3t_r} + v_2$
$s_3 = \frac{qt_3^2}{2mx_3}(V_3 - V_{2f}) + v_2t_3 = x_3$	$s_3 = \frac{qV_3t_3^2}{2mx_3} - \frac{qV_{2f}t_3^3}{6mx_3t_r} + v_2t_3 = x_3$
Region 4: $v_4 = \frac{qt_4}{mx_4}(V_4 - V_3) + v_3$	$v_4 = \frac{qt_4}{mx_4}(V_4 - V_3) + v_3$
$s_4 = \frac{qt_4^2}{2mx_4}(V_4 - V_3) + v_3t_4 = x_4$	$s_4 = \frac{qt_4^2}{2mx_4}(V_4 - V_3) + v_3t_4 = x_4$
Region 5: $v_5 = v_4$ $s_5 = v_4t_5 = x_5$	

Table 2.2 (Continued) Within Region

Region 1:

$$v_1 = \frac{qV_1}{mx_1}(t_1 - t_r) + \frac{qt_r}{mx_1}\left(\frac{V_{1f} + V_{1i}}{2}\right)t_r + v_0$$

$$s_1 = \frac{qV_1}{2mx_1}(t_1 - t_r)^2 + \left[\frac{qt_r}{mx_1}\left(\frac{V_{1f} + V_{1i}}{2}\right)t_r + v_0\right](t_1 - t_r) + \frac{qt_r^3}{6mx_1}(V_1 - V_i) + v_0 t_r$$

Region 2:

$$v_2 = \frac{q}{mx_2}(V_{2f} - V_{1f})(t_1 + t_2 - t_r) + \frac{q}{2mx_2 t_r}(V_{2f} - V_{1f} + V_{1i})(t_r - t_1)^2 - \frac{qV_{1i}}{mx_2}(t_r - t_1) + v_1$$

$$s_2 = \frac{q}{2mx_2}(V_{2f} - V_{1f})(t_1 + t_2 - t_r)^2 + v_1(t_r - t_1) + \left[\frac{q}{2mx_2 t_r}(V_{2f} - V_{1f} + V_{1i})(t_r - t_1)^2 - \frac{qV_{1i}}{mx_2}(t_r - t_1) + v_1\right](t_1 + t_2 - t_r) + \frac{q}{6mx_2 t_r}(V_{2f} - V_{1f} + V_{1i})(t_r - t_1)^3 - \frac{qV_{1f}}{2mx_2}(t_r - t_1)^2 = x_2$$

Region 3:

$$v_3 = \frac{q(V_3 - V_{2f})}{mx_3}(t_1 + t_2 + t_3 - t_r) + \frac{qV_3}{mx_3}(t_r - t_1 - t_2) - \frac{qV_{2f}}{2mx_3 t_r}(t_r - t_1 - t_2)^2 + v_2$$

$$s_3 = \frac{q(V_3 - V_{2f})}{2mx_3}(t_1 + t_2 + t_3 - t_r)^2 + (t_1 + t_2 + t_3 - t_r)\left[\frac{qV_3}{mx_3}(t_r - t_1 - t_2) - \frac{qV_{2f}}{2mx_3 t_r}(t_r - t_1 - t_2)^2 + v_2\right] + \frac{qV_3}{2mx_3}(t_r - t_1 - t_2)^2 - \frac{qV_{2f}}{6mx_3 t_r}(t_r - t_1 - t_2)^3 + v_2(t_r - t_1 - t_2) = x_3$$

Region 4:

$$v_4 = \frac{qt_4}{mx_4}(V_4 - V_3) + v_3$$

$$s_4 = \frac{qt_4^2}{2mx_4}(V_4 - V_3) + v_3 t_4 = x_4$$

Region 5:

$$v_5 = v_4$$

$$s_5 = v_4 t_5 = x_5$$

reached are given by:

$$V_1 = V_{1i} + (V_{1f} - V_{1i})t/t_r \quad (2.3)$$

$$V_2 = V_{2f}\,t/t_r \quad (2.4)$$

where t is the time expired since the initiation of the extraction pulse.

Resolution calculation

Using Equation 2.2 and those of Table 2.2, the flight time of any ion having a known initial position and velocity can be calculated. Particular distributions of initial ion positions and velocities in the source lead to a distribution of ion arrival times at the detector, and ultimately, a simulated TOFMS peak shape. In this work, normal (Gaussian) distributions of initial position and velocity were assumed. New positions and velocities were calculated for ions that moved due to the trapping field and the time lag.

Resolution, R, in mass spectrometry is defined by the following relationship:

$$R = m \,/\, \Delta m \quad (2.5)$$

where m is the mass of the ion and Δm is the peak width. The peak width is usually determined at 10% valley for magnetic mass separators and at 50% valley for time-of-flight instruments. In TOFMS, the above relationship can be rewritten as:

$$R = t \,/\, 2\Delta t = t \,/\, 2(t_2 - t_1) \quad (2.6)$$

where t is the mean flight time for ions of mass m, Δt is the peak width in units of time, and t_1 and t_2 are flight times for ions that appear on the

shoulders of the peak. Wiley and McLaren [1] have shown that the flight time in the field-free region is:

$$t = 1.02\,(2m)^{0.5}\,D\,/\,2U^{0.5} \qquad (2.7)$$

where D is the length of the field-free region and U is the total kinetic energy of the ion. Assuming that mass is not converted to energy, and flight times in the acceleration region are negligible compared to that of the field-free region, equations 2.6 and 2.7 can be reduced to:

$$R = (U_1U_2)^{0.5}\,/\,2U^{0.5}(U_2^{0.5} - U_1^{0.5}) \qquad (2.8)$$

where the subscripts represent the kinetic energies needed to produce the required arrival times on the shoulder of the peak. Notice that there is no mass dependency in Equation 2.8. Hence, in TOFMS this definition of resolution is independent of mass. However, the difference in ion arrival times between adjacent ions is a function of mass as can be discerned by the equations in Table 2.2.

Another means of relating the ability to separate ions in mass spectrometry is to identify the mass at which the height of the valley between peaks of equal intensity originating from adjacent integer m/z values exceeds a threshold percentage of the maximum intensity. All masses for which the threshold is not exceeded are said to be at least unit-mass-resolved for the specified definition of percent valley. This approach has been taken in the course of the current investigation.

In determining the percent valley between two adjacent m/z peaks it is not necessary to calculate the entire TOFMS peak shape, but only the relative intensities of the peak maximum and the valley. Flight times for

these positions on the arrival time peak shape distribution can be calculated from equations in Table 2.2. The sum of the products of the probabilities of all positions, $P(s_i,t_{of})$, and velocities, $P(v_i,t_{of})$, that result in a specified flight time yields the probability that ions have that arrival time.

$$P(tof) = \Sigma\, P(v_i,t_{of})\, P(s_i,t_{of}) \qquad (2.9)$$

This probability is directly related to the intensity observed at the detector for a particular flight time.

Intensity Calculations

The peak height of a particular m/z value is affected by the adjustment of focus parameters in a mass-dependent fashion. One reason for this mass dependency is that low m/z ions, which have higher thermal velocities than their high m/z counterparts, can actually leave the source region prior to the application of the ion extraction pulse. This causes a reduction in the number of ions available for detection. In addition, ions for which optimal focus has not been provided will result in arrival time peak shapes that have lower peak maxima and broader peak widths relative to ions that are in focus. Because the optimal focus is mass-dependent, broadening of the arrival time peak shape is also mass-dependent.

As a consequence of the mass-dependent relationship between focus parameters and the peak intensity, a skew in the mass spectral peak intensities can be observed when large ranges of m/z values are monitored. This is especially apparent when using algorithms based on peak height rather than area. In the definition of useful m/z windows, it is therefore necessary to include a threshold for the loss of peak height as well as one for the loss of mass resolution.

Ions that are calculated to be outside of the ionization region before or after the application of the time lag are ignored. In this manner the contribution of ions that have left the source prior to extraction have been considered. Other intensity calculations are based on the peak height, or the probability at the most probable arrival time.

Simulation

The simulation used for this work was written in FORTRAN-77 on a MicroVAX II. The code consists of a main program, LIMRES, and nine subprograms and functions. A source code listing of this program is included as Appendix I of this document. Several of the algorithms used in this program are modifications to programs obtained from George Yefchak or from reference 9. The source of these algorithms has been noted in the code.

The main program is used to set the parameters used in the calculations and to loop through variables. These parameters include voltages and distances in the various regions of the instrument, ion m/z value, time lag, ramp time, and desired limits of resolution and intensity. Through subroutine and function calls, this program calculates flight times, resolution, and intensities of two adjacent m/z value peaks of equal probability. The main program is also used to write the results of the calculations to a file in Cricket Graph [10] format. This program was altered frequently to incorporate features that were desired in the output. Appendix I contains a version of this program which looped through mass, time lag, and ion focus in acquiring data.

LIMRES performs its functions through calls to CALTOF and MAXMIN. CALTOF is the subroutine in which ion flight times are

calculated. This routine is based on Equation 2.2 and the solutions with respect to time of equations in Table 2.2. This requires the evaluation of quadratic or cubic solutions using QDSOL or CUBSOL, respectively. The routine accepts variables for the initial position, initial velocity, and m/z value to calculate flight time in μs.

MAXMIN is the subroutine that is used to find the peak maximum and the height of the valley. This routine receives boundary flight times and returns intensities for the valley and peak heights. The peak shape distribution resulting from Gaussian distributions of initial positions and velocities is not necessarily a Gaussian distribution, and hence, this routine was written to examine several points across the distribution of arrival times. This is done through calls to TPROB and SIMPS. The latter function calculates the area of a peak through a Simpson's rule approximation.

The subprogram TPROB is used to calculate the probabilities or intensities of a particular ion arrival time. This routine loops through possible spatial positions in the source and calculates the velocity needed to achieve the desired flight time through a call to VELCAL. Initial positions and velocities are then calculated to compensate for movement during the time lag. Through calls to PRBLTY, the probabilities of the initial positions and velocities are calculated. Equation 2.9 is then implemented to determine the total probability as the sum of the products of individual probabilities of initial positions and velocities.

PRBLTY is the function that returns the probability of occurrence of an event. It assumes a normal (Gaussian) distribution of events. Normalization of the function was not included so that the maximum intensity obtained is 1.

VELCAL is the subroutine that is used to calculate the initial velocity of an ion from its arrival time and m/z value. A plot of initial velocity versus ion flight times to the detector, such as the one presented as Figure 2.3, is approximately linear with the intercept being a function of the ion's initial position and m/z value. Deviation from linearity is observed to occur as the initial velocity differs significantly from 0 m/s. VELCAL uses a linear approximation between small intervals of velocity to determine the initial velocity. This is done with the aid of function calls to LINE which is used to compute the slope and intercept of a line. The interval approach was used instead of root finding algorithms to speed up the calculations while minimizing deviation from the correct result that would be observed if a single interval were used. In regions of significant deviation from linearity, the probability of occurrence for the initial velocities is small enough that weighting factors make these errors insignificant. For example, the probability that m/z 10 would have a velocity of 3000 m/s from thermal energy is 0.000024. This probability drops further as the value of m/z is increased. The weighting of such a small probability with those of smaller velocities makes this value and any inherent errors insignificant as long as a sufficiently large number of samples are obtained.

Results and Discussion

Effect of time lag

The effect of time lag on the peak shape is illustrated in Figure 2.4. This figure includes some of the contribution to the peak intensity from a peak of equal intensity at the next higher integer m/z value in order to determine the height of the valley between the two peaks. As the time lag approaches its optimum value, the peaks get narrower and more intense with a decrease in the height of the valley between adjacent masses. Additionally,

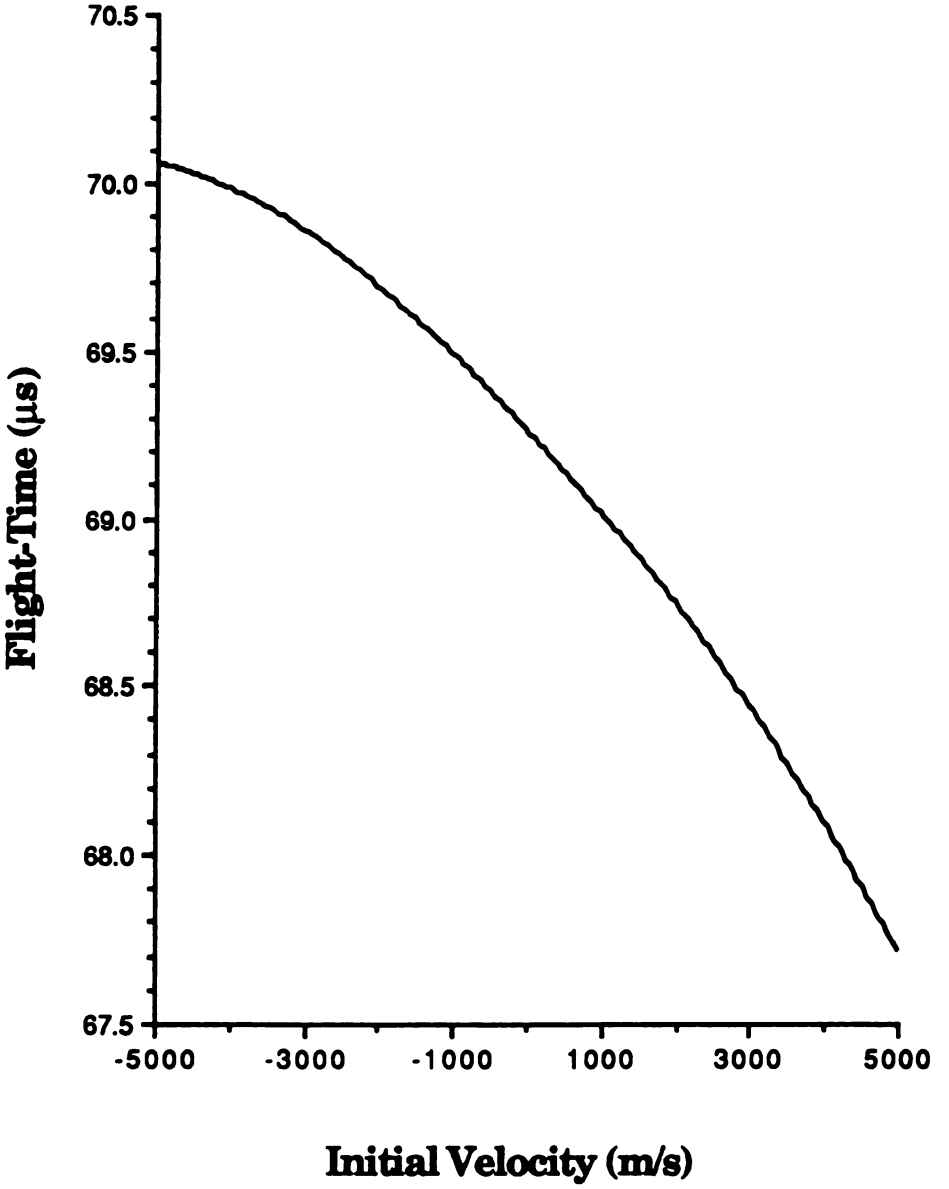

Figure 2.3. The relationship between initial velocity and ion arrival time at the detector for m/z 500.

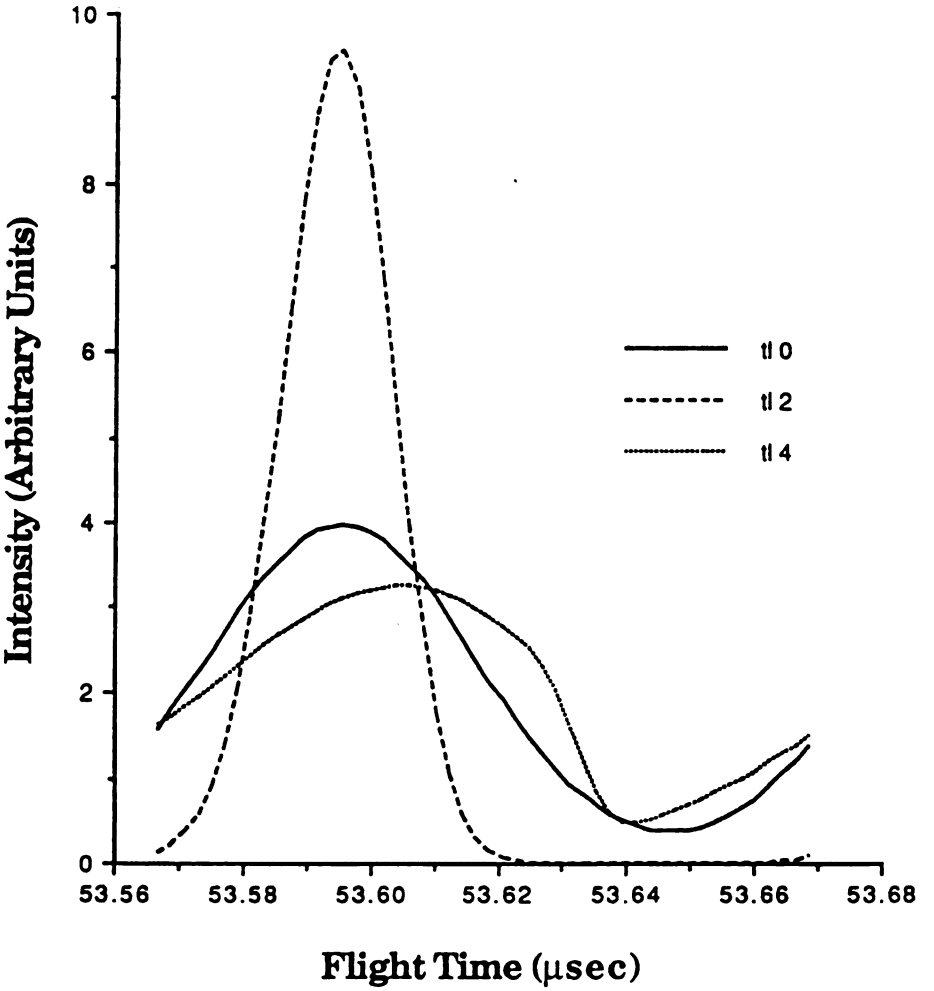

Figure 2.4. Simulated peak shapes for m/z 500 at different values of time lag.

as the time lag is increased beyond the optimum, the peak shape is skewed towards longer flight times.

The effect of time lag on the peak intensity is demonstrated in Figure 2.5. In this figure, the relationship between peak intensity and time lag is plotted for ions of several different m/z values. The lightest ions exhibit the largest intensity. This is an artifact of the narrower peak widths found for the lightest ions. The optimum intensity for each ion occurs at higher values of time lag as the m/z value increases. This phenomenon has been observed in data from the instrument as shown in Table 2.3. These results are also in agreement with those of Wiley and McLaren [1] which demonstrated that the optimum time lag is proportional to the square root of the ion's mass. Data in Table 2.3 fit the equation:

$$t_{lag} = 0.0956\,(m/z)^{0.5} + 0.139 \qquad (2.10)$$

where t_{lag} is the time lag in μsec. The regression coefficient for fitting these data to Equation 2.10 is 0.988 and is due in part to a difficulty in reading accurate time lags from an oscilloscope. Constants in this equation are a function of the voltages applied to the extraction grids.

Table 2.3. Experimental Optimum Time Lag

m/z	Time Lag
69	0.3 μsec
100	1.1 μsec
131	1.3 μsec
181	1.4 μsec
231	1.6 μsec
281	1.6 μsec
331	1.9 μsec

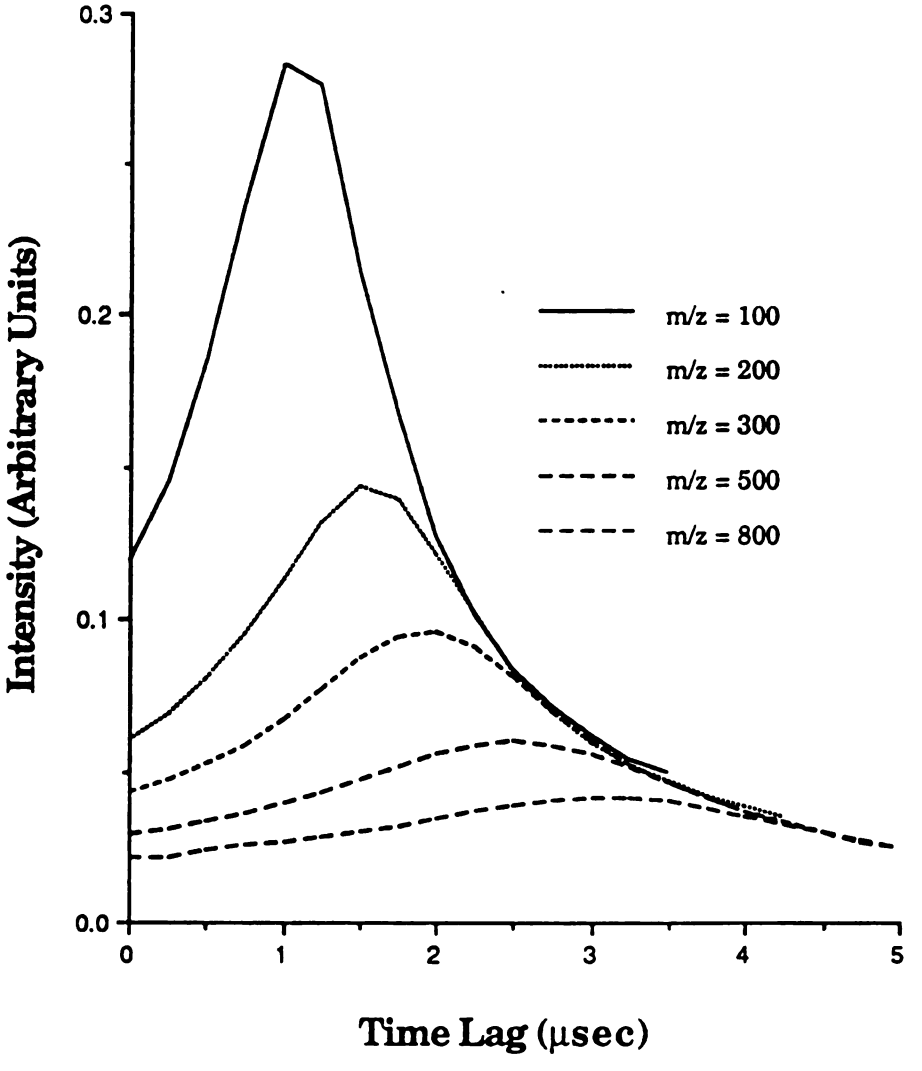

Figure 2.5. The dependence of peak height on time lag and mass.

A plot of time lag versus percent valley for a particular m/z ion passes through a minimum at the optimum time lag for that m/z value. An example of such a plot for several values of m/z is included as Figure 2.6. As previously noted, the optimum time lag increases as a function of m/z. This figure can be used to identify the values of time lag at which ions will have at least unit-mass-resolution. For example, at least unit-mass-resolution is achieved at 10% valley for m/z 300 at all values of time lag below 3.8 μsec. Unit-mass-resolution is achieved for ions of m/z 700 only for values of time lag between 2.5 and 3.2 μsec. Minima in Figure 2.6 also correspond well with experimentally observed optimum time lags in Table 2.3, agreeing to within 0.15 μsec.

Figure 2.7 is a comparison plot of time lag versus percent valley for experimentally observed values from the m/z 502 ion in perfluorotributylamine relative to calculated values for m/z 500. Except for one point, the calculated curve lies within the error of the experimental measurements. Excellent agreement between the simulation and the instrument is observed for those values of time lag which result in sharp peaks (adequate focus). The calculations result in a systematic difference in the height of the valley relative to experimental values as the resolution is significantly degraded. This may be an artifact of the ability to accurately measure peak and valley heights in the experimental data when significant overlap occurs. Difficulties in correlating the experimental data to the model at low values of time lag may be due to errors in the model's ability to mimic ion events occuring immediately upon the application of the extraction pulse. In addition, the model does not account for ion repulsion or fringing fields which do occur in the instrument.

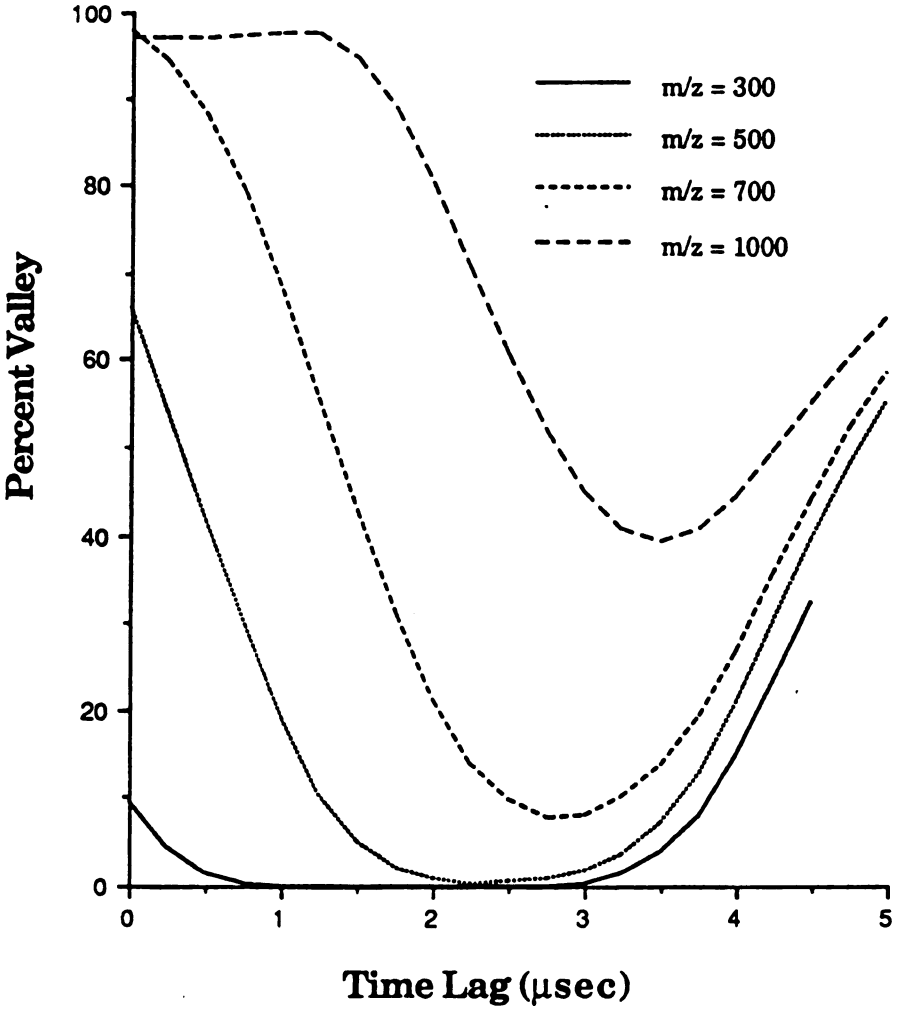

Figure 2.6. The calculated effect of time lag on resolution.

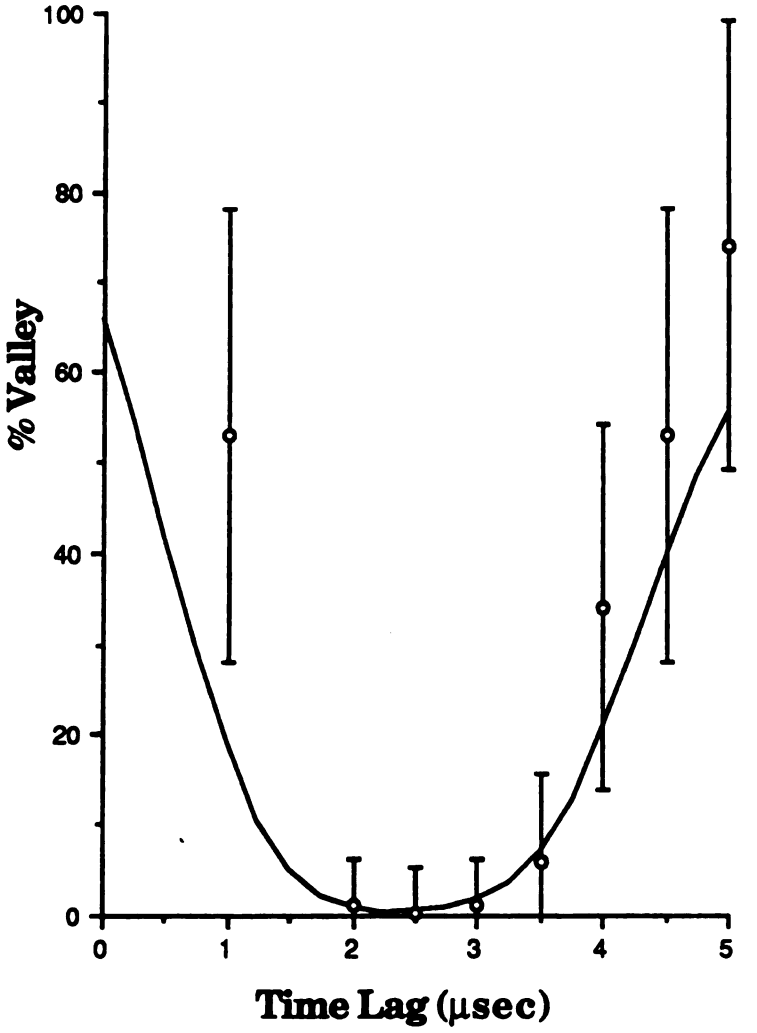

Figure 2.7. The effect of time lag on resolution. Calculated values for m/z 500 are plotted as a continuous curve. Points indicate experimental values for the m/z 502 peak from perfluorotributylamine.

The useable m/z windows are bounded by the intensity and resolution limits required to obtain satisfactory signal. The definition of these boundaries on a plot of time lag setting versus. m/z value will identify the usable mass range for a given time lag setting or the appropriate time lag settings required to cover a given mass range. Such a plot is included as Figure 2.8. In this figure, a resolution threshold of 10% valley and an intensity threshold of 90% were chosen as acceptable limits. All m/z values to the left of the 10% valley boundary have at least unit-mass-resolution. At low values of m/z, the arrival times between integer m/z values is so large that unit mass resolution is always obtained. All points between the intensity boundaries have no greater than a 10% loss in the peak height. The area defined by these three boundary curves gives the useful mass window for each value of time lag. The curve between the intensity boundary curves of Figure 2.8 provides the optimum time lag as a function of the ion's m/z value.

It is now possible to use Figure 2.8 to determine the window of acceptance for monitoring multiple ions from a single extraction pulse of a TOFMS source. For example, to collect a spectrum from m/z 50 to 700 would require the use of three different time lags with their inherent functional mass windows. Values of time lag used would be 1.0, 1.5, and 2.8 μs and would cover m/z ranges between 50 to 150, 150 to 300, and 300 to 700 Daltons, respectively. Multiplexing these windows together from successive extraction pulses would produce a complete mass spectrum with each peak in adequate focus. The price of multiplexing these 3 windows relative to using an array detection scheme in which all ions are in focus is a factor of 3 loss in sensitivity and a factor of 1.7 loss in signal-to-noise (S/N) ratio. Compared to a scanning detection method with a 5 ns window, the use of these 3 windows

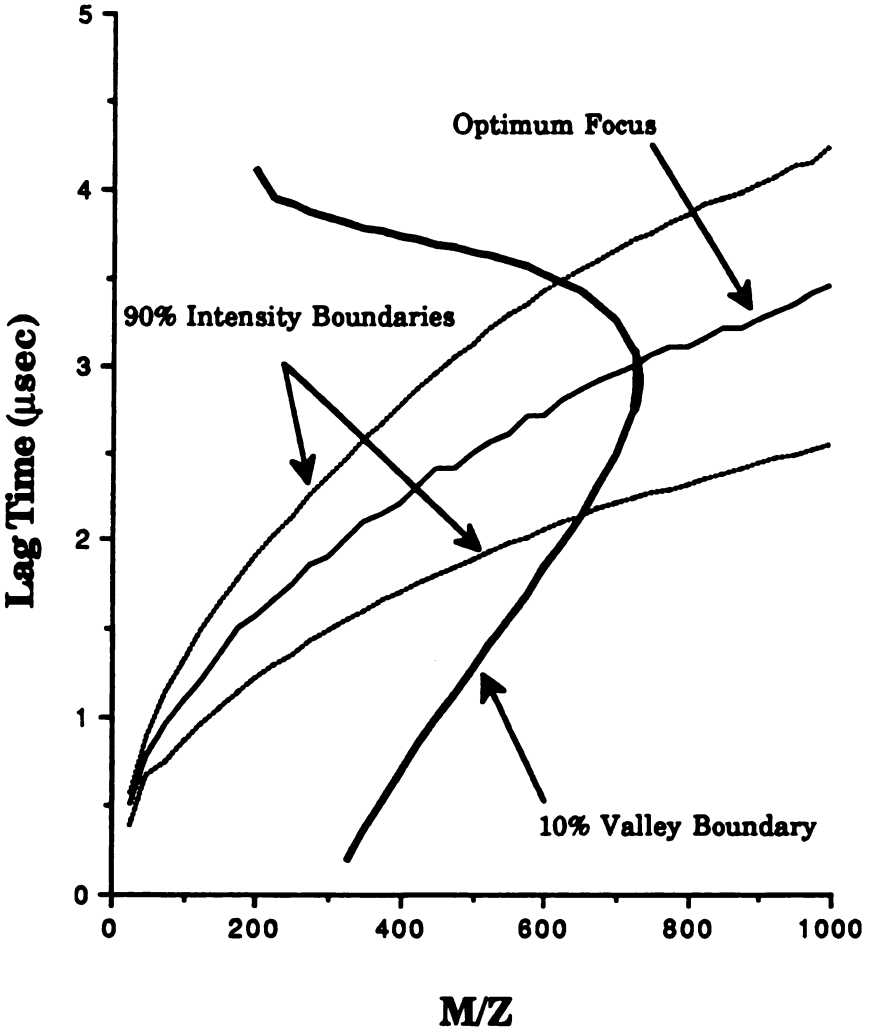

Figure 2.8. Working curve for acceptable signals. Ions to the left of the resolution curve give unit-mass-resolution with less than a 10% valley. Ions between the intensity curves loose no more than 10% of their peak height. The curve in the center gives the optimum time lag for each m/z value.

gives a factor of 4000 increase in sensitivity and a factor of 63 increase in the S/N ratio.

Effect of extraction grid potentials on ion focus

Isomass ions with identical initial energies that are in different positions in the source when the extraction pulse is applied will acquire different energies, and hence, velocities as they leave the source. Ions that travel farthest in the source region will have the highest energy and velocity, but will be the last to leave the source. They catch up to the slower ions at the space focus plane. The distance of this space focus plane from the source is a function of the potential applied to the first grid, the ion focus potential. Ideally, this plane is located at the detector surface. When it is not located at the detector surface, broadening and a distortion of peak shapes can be expected. Experimentally, improper adjustment of the ion focus voltage presents itself as a loss of peak height, a broadening of the peak, and a distortion of the peak shape.

A plot of ion focus voltage against percent valley should have a minimum at the optimum value of the extraction potential. Such a plot is included as Figure 2.9 for a m/z value of 500. This figure also shows that the optimum ion focus voltage is a function of the time lag, with larger time lags requiring a shift to lower ion focus voltages. In Chapter 1 the energy obtained by an ion as it leaves the source was visualized as the height of the ion on the potential hill. The ion focus potential sets the maximum height of this hill and hence its slope. Large values of ion focus potential require smaller delay times to permit ions to migrate to the requisite new positions for proper spatial focusing than do small potentials. This results in large ion focus potentials requiring small values of time lag while small ion focus

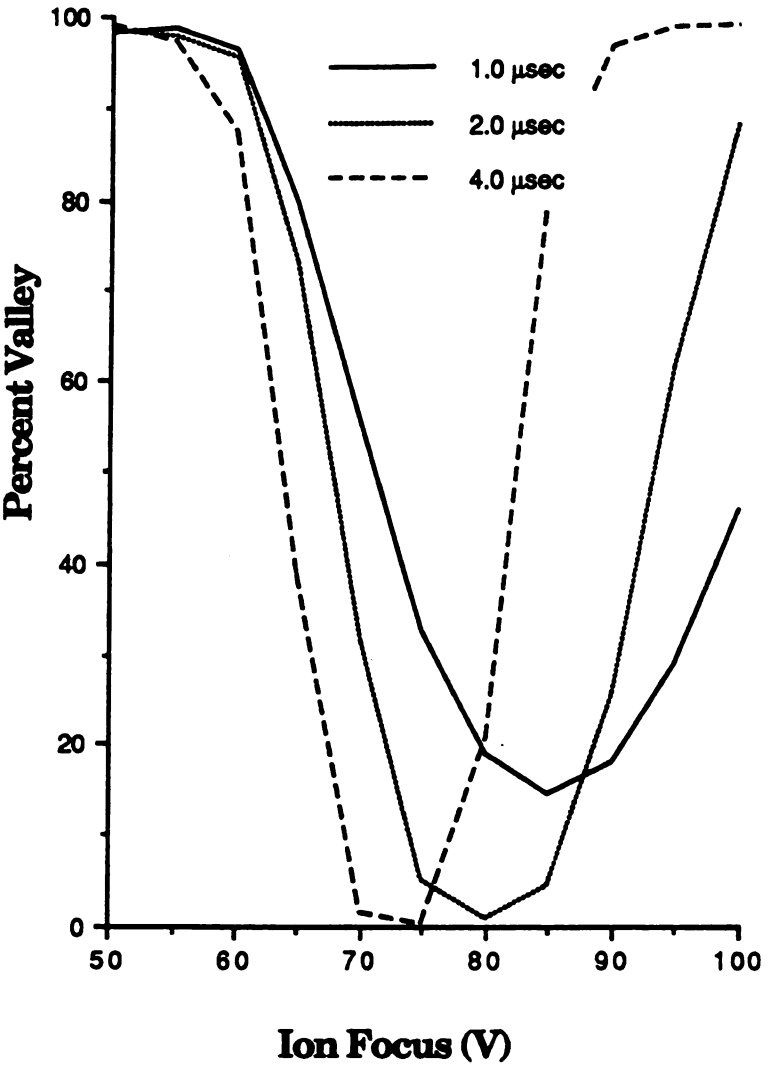

Figure 2.9: Resolution as a function of the ion focus potential for m/z 500.

potentials require large values of time lag. This phenomenon is illustrated in Figure 2.10, where time lag is plotted against the percent valley for several different values of ion focus. In this figure it becomes apparent that the window of acceptable time lags is smaller for the larger ion focus voltages while the smaller voltages require time lags larger than are readily available on the commercial instrument. Additionally, high values of the time lag will increase the probability that low m/z ions have left the source prior to the application of the extraction potential, which would result in an undesirable skew in the mass spectra.

The selection of an optimum ion focus potential is a trade off between the size of the mass window at a particular time lag value and the desired total mass range for the analysis, as illustrated in Fig 2.11. This figure shows the effect of ion focus potential on the shapes of the resolution and intensity limiting boundary curves for the same threshold values as used for Figure 2.8. Increasing the value of the ion focus potential causes the optimum focus to occur at lower values of time lag. This causes a desirable leveling off of the curves which define the intensity window, making the degradation in signal intensity less prominent across wider mass ranges. At the same time, however, the increase in ion focus potential causes a shifting of the resolution curve to lower values of time lag and m/z. For example, at an ion focus potential of 75 V, a time lag of 2.5 μsec has a practical mass range between about m/z 150 and 350 for a 200 Dalton window size. Setting the ion focus voltage to 77 V, this mass range changes to roughly 200 to 500 with a window size of 300 Daltons. Both of these voltages cause the window size to be determined only by the intensity threshold. Using an ion focus potential of 80 V, the intensity limits at a time lag of 2.5 μsec provide an adequate signal intensity over the 750 Dalton window between m/z values of

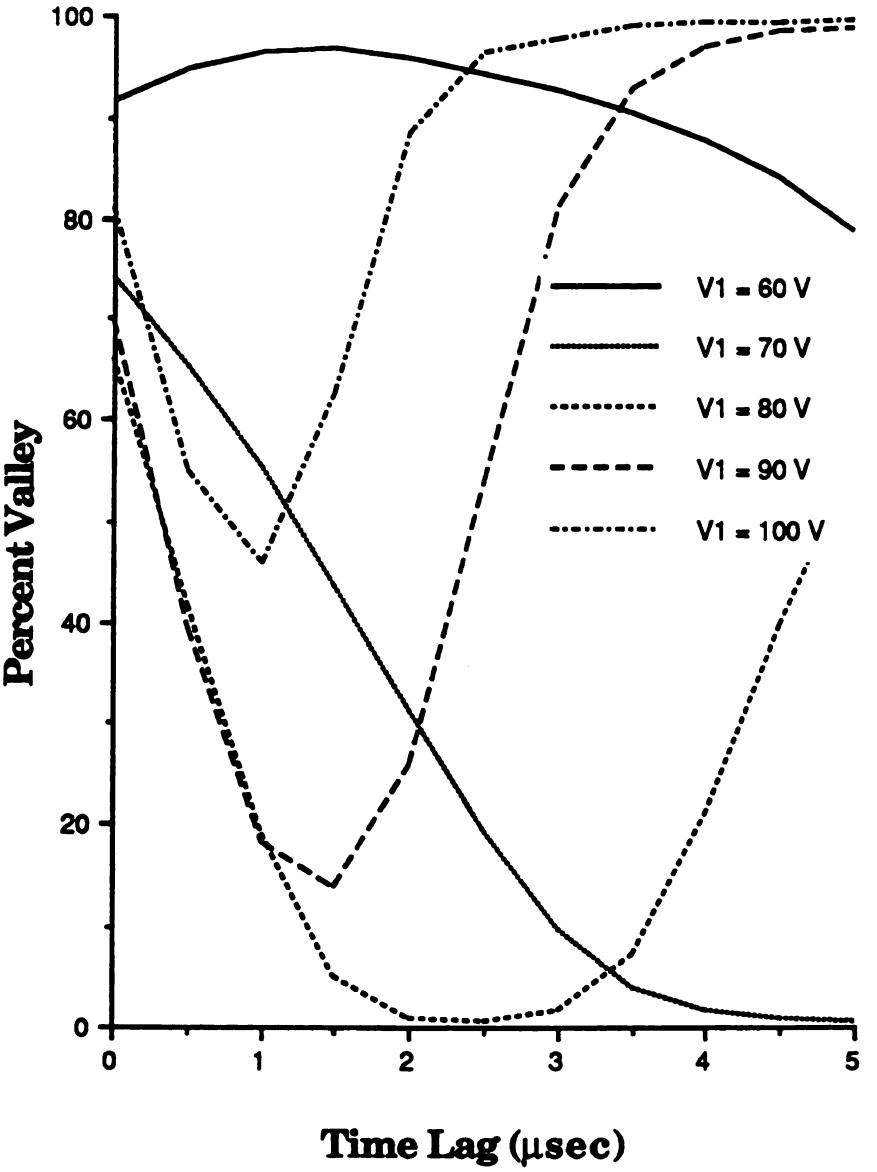

Figure 2.10. Interdependence between resolution, time lag, and ion focus

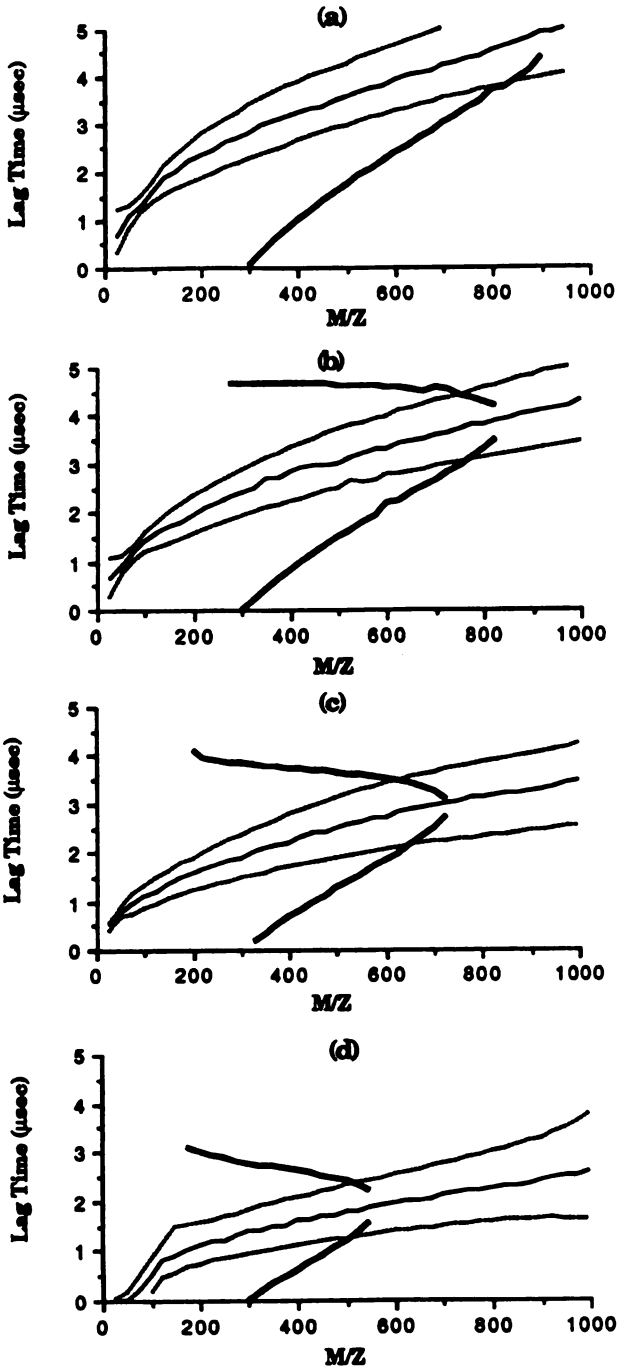

Figure 2.11. Working curves for ion focus values of (a) 75 V, (b) 77 V, (c) 80 V, and (d) 85 V. The V_2 voltage used was 215 V.

225 and 950. However, the resolution threshold has moved down into this window, restricting the upper limit to a m/z value of about 700. The window size is thus only about 475 Daltons. At an ion focus voltage of 85 V and a time lag of 2.5 μsec, the resolution cutoff occurs before entering the acceptable intensity range, leaving all ions outside of the acceptable limits of signal degradation.

The ion-accelerating pulse is applied to the second grid concurrently with the ion focus pulse applied to the first grid (V_1 and V_2 in Figure 2.2). The effect of the potential applied to the second grid on ion resolution is demonstrated in Figure 2.12. This potential has a minimal effect on low m/z ions since they require small values of time lag for optimal focus. Ions that require larger values of time lag will benefit from the increased window of acceptable time lags from using higher V_2 potentials.

The effect of the V_2 potential on the size of the mass windows for selected values of time lag and a constant value of the ion focus potential is illustrated in Figure 2.13. This figure was generated using the same resolution and intensity boundaries as used to produce Figures 2.8 and 2.11. The observed effect is similar to that of the ion focus voltage. Lower V_2 voltages lower the slope of the optimum value and intensity limiting curves (dotted lines) while also causing the 10% valley limiting curve (solid line) to be pulled towards the plot origin. A trade off is therefore needed to get the largest m/z range and the widest m/z window sizes. This effect is not as severe as that caused by the ion focus potential, requiring much larger changes in potential to produce noticeable effects.

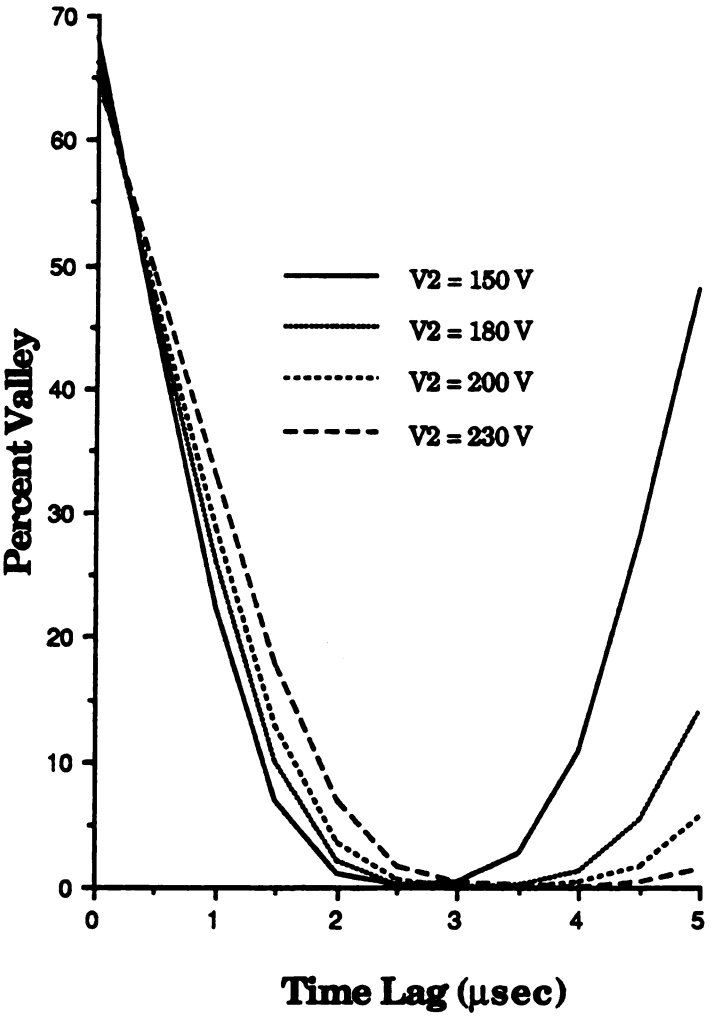

Figure 2.12. Resolution as a function of time lag and V_2 potential.

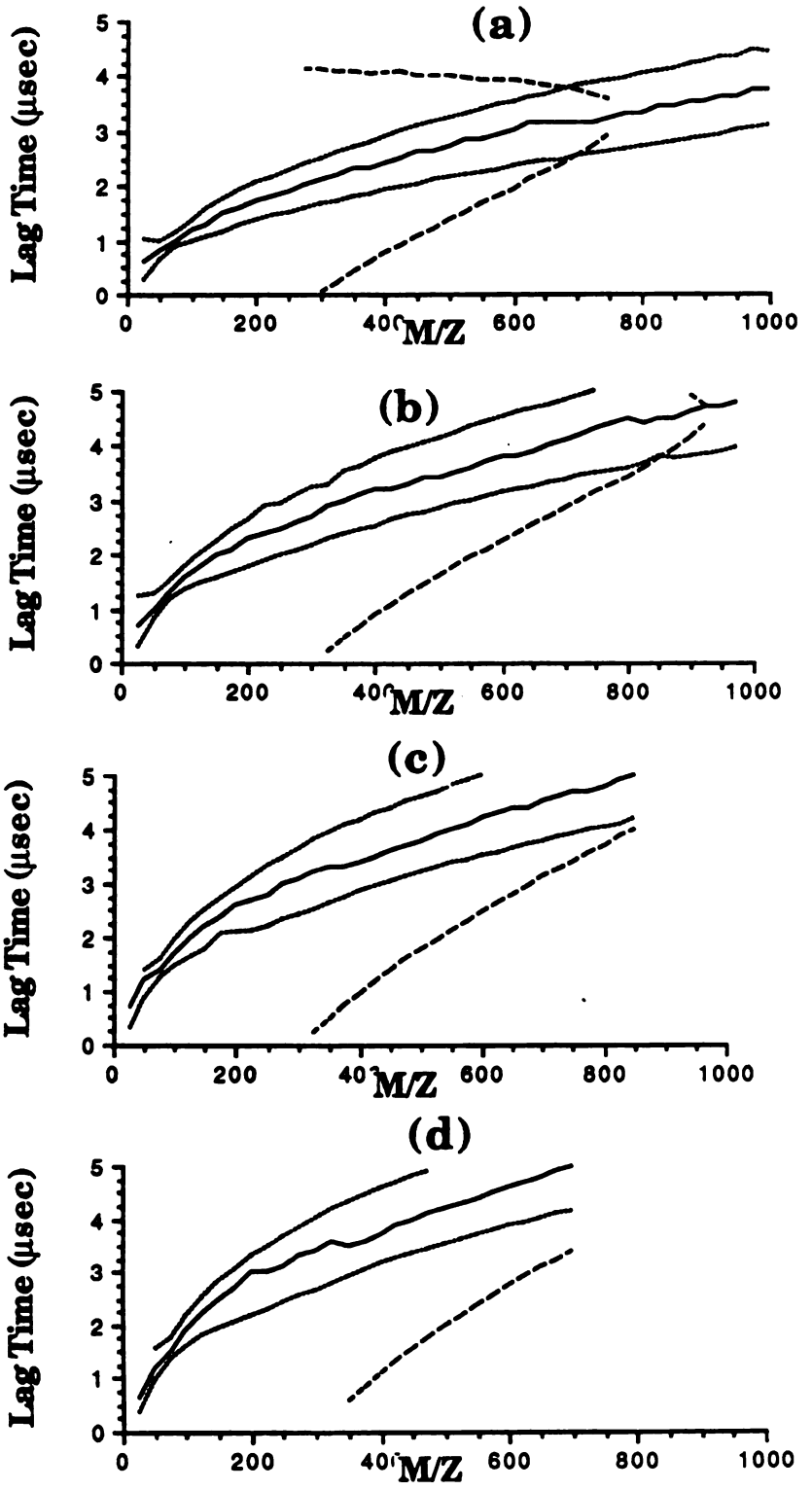

Figure 2.13. Working curves for V_2 values of (a) 150 V, (b) 200 V, (c) 225 V, and (d) 250 V. The ion focus voltage used was 80 V.

Effect of ramp time

Use of digital simulations instead of instrumental experiments permits the examination of the effects of changing parameters that are difficult to manipulate on an actual instrument. One such case is the examination of the effects caused by non-ideal extraction pulses. Experimental examination of this effect would require instrument modification. As described in the theoretical section of this chapter, this case is accommodated within the simulation through the assumption of a linear extraction potential ramp in the derivation of the equations of motion of ions in the instrument. The duration of the ramp, t_r, is an adjustable parameter in the simulation.

Figure 2.14 shows the effect on resolution of using different ramp times. Increasing the ramp time of the ion extraction pulse produces a minor increase in the resolution for low values of time lag. Since this effect is similar to that of increasing the time lag, longer values of t_r require lower values of time lag to obtain the same focus. It is interesting to note that this phenomenon results in an apparent enhancement in resolution as the rise time of the ion extraction pulse increases.

The effect of the ramp time on the plot used to determine the size of the mass windows is minor. Increasing the ramp time causes the curves that delimit resolution and intensity thresholds to maintain their shape and slope, but shift to lower time lags. This outcome is a result of the fact that at higher values of the ramp time, ions spend more time in the ionization region of the source and hence have more time to be displaced from their original positions as a result of their thermal velocities. More time is required for the extraction potential to overcome the initial ion energies and direct the ions towards the detector. This ion displacement is similar to that occurring as a

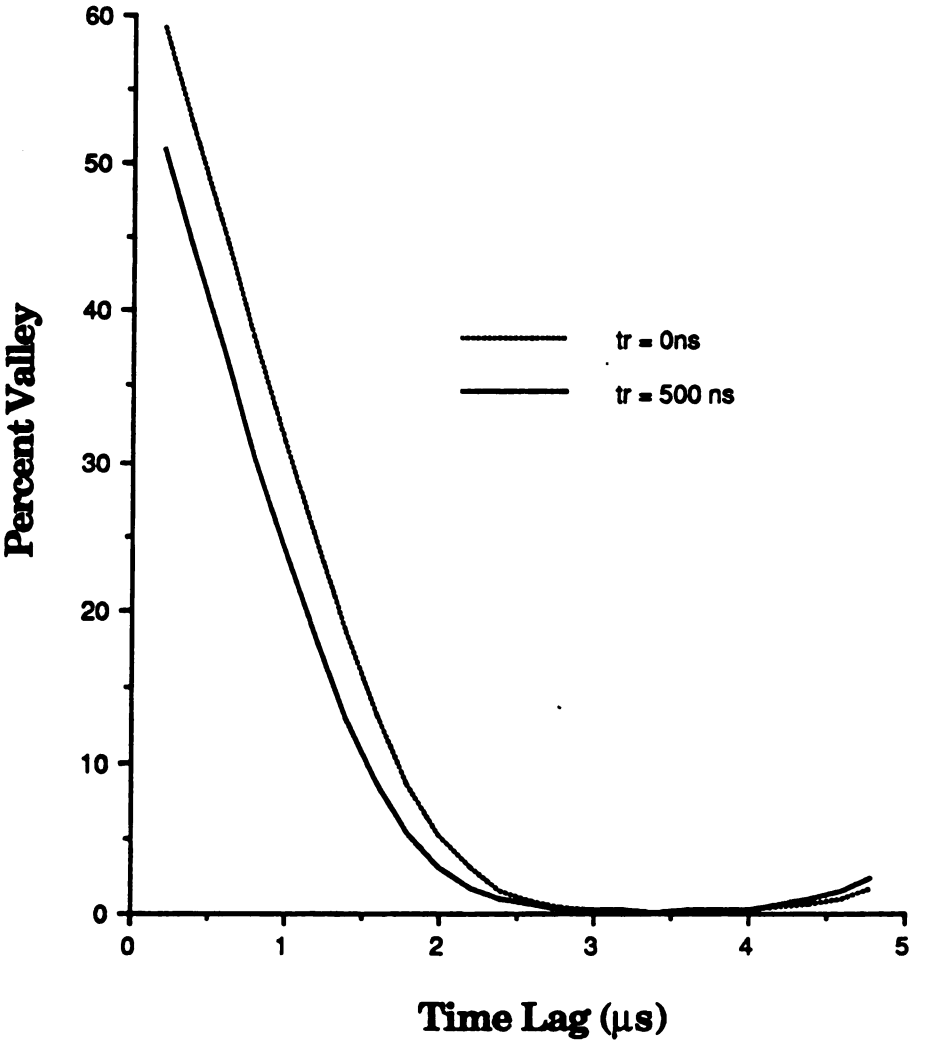

Figure 2.14. Effect of ramp time on optimum time lag for m/z 500.

result of the time lag, and therefore, requires lower values of time lag to obtain the necessary ion separation distance in the source.

Conclusions

In TOFMS, mass windows of acceptable signal quality for particular settings of time lag can now be defined for use with detection schemes that involve monitoring more than one m/z value from each extraction pulse. The boundaries of these mass windows are dependent upon many instrumental parameters and are instrument specific. Parameters that are most likely to affect the size of the windows are the time lag and the ion focus potential (V_1). Nonideal extraction pulse shapes have limited effect on the size of the mass windows, being manifested instead as a slight diminution to the requisite time lag.

The width of functional mass windows is limited by intensity boundaries throughout the low mass range. Resolution boundaries only become a factor at high masses. This fact can be used to help generate plots similar to those of Figs. 2.8, 2.11. and 2.13 for other TOFMS instruments and parameters. It is possible to derive the intensity boundaries by optimizing time lag for a particular peak followed by adjustment of the time lag until the peak intensity has been reduced by a factor of 10%. Performing this operation for several m/z values will result in the collection of sufficient data to generate the intensity boundaries. As long as the resolution boundary is not exceeded, these boundary curves will define the useful mass ranges.

An examination of data used to generate the working curves in Figs. 2.8, 2.11, and 2.13 has revealed a means to estimate the size of the functional mass window around a selected m/z value. For those cases where resolution is not the limiting factor and the ion focus voltage is close to its optimum

value, the upper limit on the window is a factor of between 1.55 and 1.70 of the m/z value that is in optimum focus. The lower limit is between a factor of 0.65 and 0.75 of the optimum m/z value. This approximation fails for m/z values below 100 and for cases where resolution determines the upper boundary. Intensity thresholds other than 90% of the optimum intensity will also alter this approximation. In addition, these estimates may not be valid if instrumental parameters are not the same as those listed in Table 2.1.

The TOFMS-time-array detection system was used to collect the spectra of perfluorotributylamine listed in Table 2.4. A time lag value of 0.8 μs was used for Case A, which provided an optimal focus for m/z 69 and a mass window of acceptable intensities from m/z values of 40 to 110. Using time lag values of 0.9, 1.5, and 2.0 μs and windows of 50-100, 100-300, and 225-575 respectively, intensities for Case B were put together to obtain a spectrum in which all peaks are focused within acceptable limits of intensity and resolution degradation. The Case B spectrum has a slight decrease in intensities at low masses and a significant increase in intensities at high masses relative to the Case A spectrum.

Table 2.4. Mass Spectral Intensities of Perfluorotributylamine

m/z	% Relative Intensity	
	Case A	Case B
28	3.1	2.8
31	0.39	0.37
32	0.83	0.81
40	0.08	0.07
41	0.05	0.05
42	0.01	0.01
43	0.29	0.28
44	0.04	0.04
50	0.24	0.24
51	0.08	0.08
55	0.01	0.01
57	0.37	0.37
58	0.04	0.04
69	100.	100.
70	1.1	1.1
71	0.16	0.16
81	0.11	0.11
85	0.07	0.07
93	0.40	0.40
95	0.08	0.14
100	8.8	9.4
101	0.10	0.16
112	0.18	0.29
113	0.01	0.03
114	1.5	1.9
119	4.6	4.8
131	16.	18.
132	0.43	0.48
145	0.09	0.11
150	0.55	0.98
162	0.03	0.08
164	0.14	0.22
169	0.80	1.2
176	0.18	0.30
181	0.42	0.60
186	0.04	0.12
214	0.05	0.09
219	25.	30.
220		0.14
226	0.03	0.11
231	0.02	0.11
264	2.4	4.6
464		0.45
502	1.2	2.1
503		0.11

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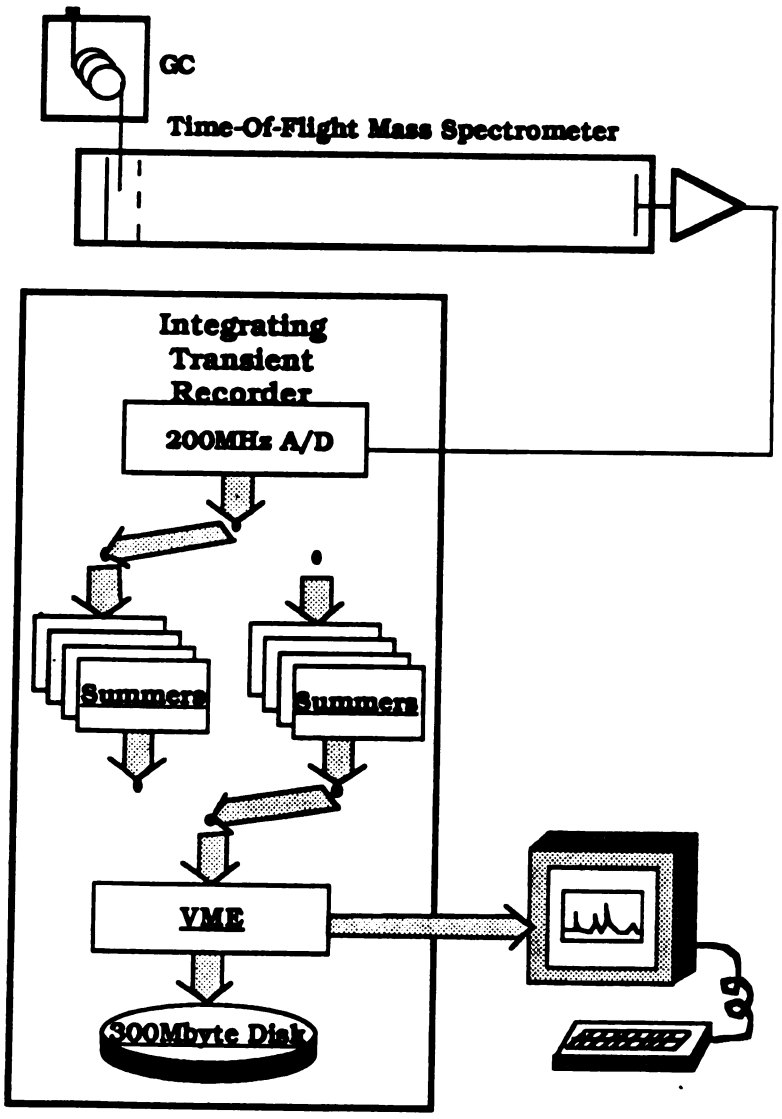
CHAPTER 3:
APPLICATION OF TIME-ARRAY DETECTION TO CAPILLARY COLUMN GC-TOFMS

INTRODUCTION

As previously discussed, time-array detection should have several advantages over scanning detection schemes. Among these are the abilities to accurately reproduce the chromatographic elution profile, to obtain unskewed spectra of rapidly changing source concentrations as in gas chromatographic effluent, to improve the signal to noise ratio of the mass spectral signal, to optimize the chromatography for reduced analysis times, and to collect all the information generated during the analysis. This chapter demonstrates that the time-array apparatus at Michigan State University has these advantages and, hence, meets the demands placed on mass spectrometers when used as detectors for high resolution capillary gas chromatography.

EXPERIMENTAL

The time-array detection (TAD) system used in this research is shown schematically in Figure 3.1. It consists of a gas chromatograph, a time-of-flight mass spectrometer, and an integrating transient recorder.



3.1. Schematic diagram of the time-array detection system.

Gas Chromatography

A Hewlett-Packard 5790 gas chromatograph was used in the split injection mode. A 22 m length of 0.25 μm I.D. fused silica column coated with 0.25 mm SE-54 was used for the separations. The column was directly interfaced to the mass spectrometer. Column temperature programming was optimized to obtain the desired information in the minimum time.

Mass Spectrometry

The instrument used for this work was a CVC 2000 time-of-flight mass spectrometer equipped with a conventional 2 m linear flight tube. This is the same instrument that was modeled in the previous chapter. The signal from the detector was amplified by a Comlinear Corp. E220 preamplifier prior to processing by the ITR. The original potentiometers controlling the values of time lag and ion focus voltage were replaced with 10-turn potentiometers to improve the precision with which these values could be set. Calibration curves for these potentiometers are included as Figures 3.2 and 3.3.

The CVC 2000 was originally equipped with a magnetic electron multiplier (MEM) detector. This detector exhibited poor sensitivity and was subject to noise and ringing from the gating anodes. Removing the gating electronics and grounding all extraneous plates improved the noise problems, but sensitivity was still inadequate. It also became difficult to obtain expendable components for these detectors. The detector was replaced with a Galileo FTD-2003 channel plate electron multiplier (CEMA). A new flange was ordered to fit the flight tube and modified to pass the required voltages to the CEMA with 2 extra electrical feedthroughs for future use. Threaded holes were included on the inner surface of the flange in case supports would

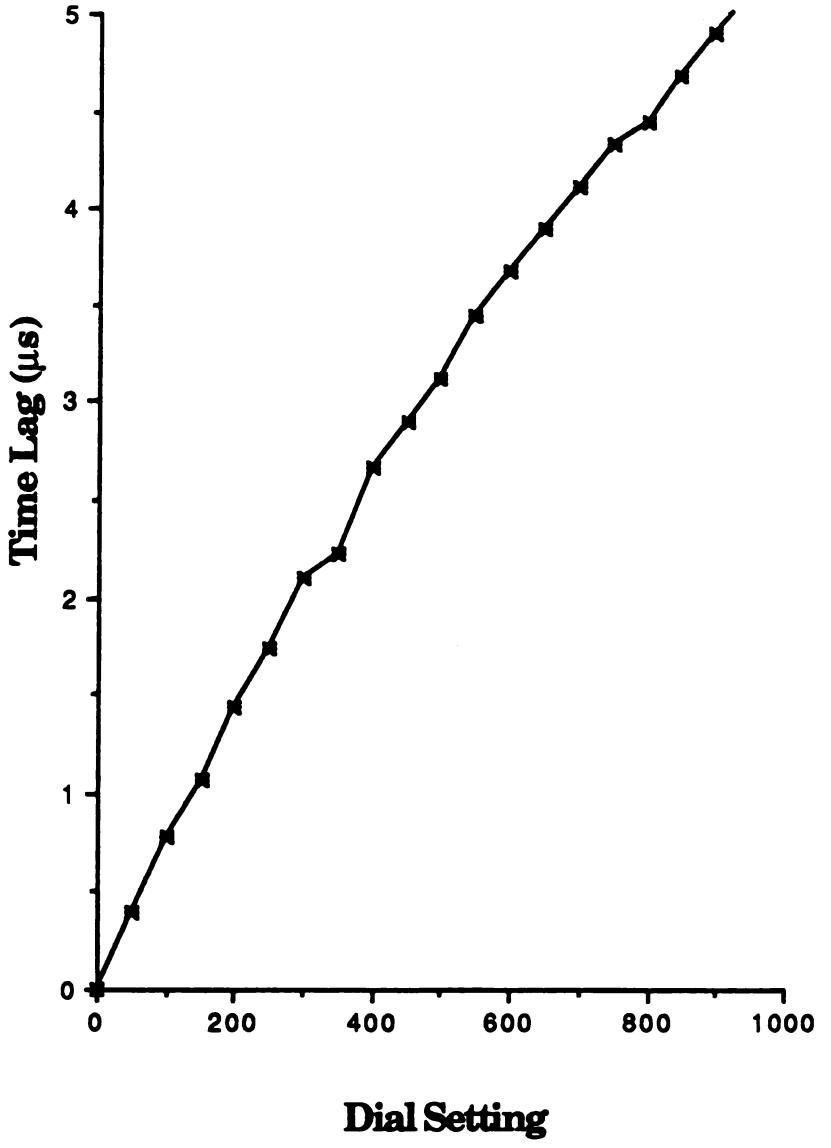


Figure 3.2. Calibration curve for the time lag potentiometer.

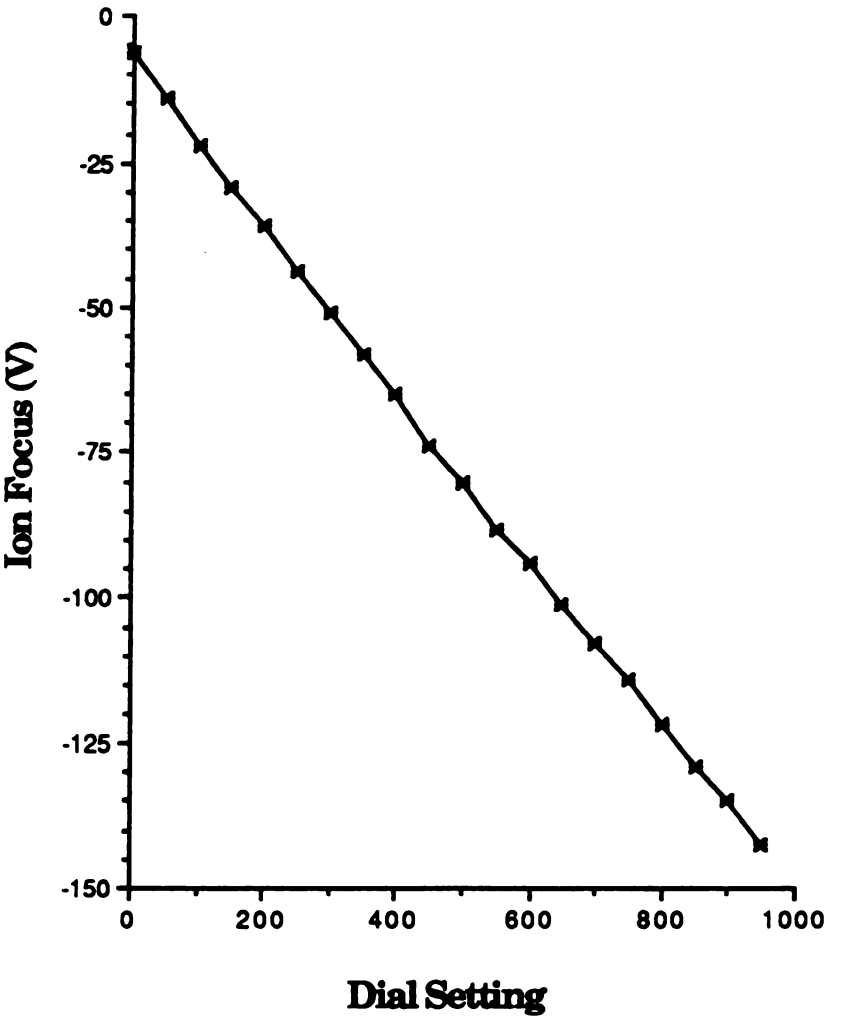


Figure 3.3. Calibration curve for the ion focus potentiometer.

be needed for future modifications. The voltage applied to the front surface of the CEMA was obtained by running the high voltage line applied to cathode number 1 (pin 13, -2837 V) from the old detector to the CEMA. Voltages for the back surface of the CEMA were pulled from the line that had previously supplied cathode number 2 (pin 11, -1000 to -1500 V) on the old detector. In this way, the CVC electronics were able to provide power and an adjustable gain to the new detector. This also permits control of the detector gain using controls already on the instrument control panel. However, the gain control now works in reverse with a setting of 11 providing the least gain and a setting of 1 providing the maximum gain. Voltages applied to the rear surface of the CEMA are listed in table 3.1.

Table 3.1. Gain Voltages Applied to the Rear Surface of the CEMA.

Gain Setting	Voltage Applied
1	-995
2	-992
3	-1039
4	-1085
5	-1133
6	-1179
7	-1226
8	-1273
9	-1320
10	-1366
11	-1414

Replacement of the MEM detector with the CEMA necessitated a change in the mechanism for scanning the mass spectrum. The scanner circuitry was disconnected and replaced with a model 162 boxcar averager from EG&G Princeton Applied Research. Use of this boxcar enabled the acquisition of time-slice (scanned) spectra.

The integrating transient recorder provides its own start pulse in order to synchronize the data collection. It was necessary to modify the mass

spectrometer's electronics (pulse 2 card) to accept such a signal and use it to pulse the electron beam and extraction of ions from the source. An opto-isolator was used in the circuitry to minimize noise on the trigger pulse that could be carried between the instrument and the ITR. It was also desirable to permit the instrument to occasionally operate from its own clock when performing time-slice detection, so a switch was placed on the pulse 2 card to permit this operation.

As mentioned in the previous chapter, ion focusing in time-of-flight mass spectrometry is a function of mass. Selection of the appropriate focus parameters will result in mass ranges in which acceptable ion signals can be obtained. Unless stated otherwise, data in this chapter were obtained with an optimum focus for m/z 71 (a time lag of 0.9 μs). This value of time lag provides acceptable signal for ions between 50 and 120 Daltons. Compounds analyzed were generally low molecular weight species for which this mass range was adequate.

Integrating Transient Recorder

The ITR was designed and constructed at Michigan State University. As the ITR has been described elsewhere [1,2,3], it will be discussed only briefly here. Signals from the mass spectrometer are sampled every 5 ns by a LeCroy TR8828B 200 MHz A/D converter, dividing the spectrum into 16,000 time bins. This permits collection of the entire mass spectrum with sufficient separation of the 20 ns wide mass spectral peaks. High speed emitter coupled logic (ECL) 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. Meanwhile, the other bank passes data from the previous

summed scan to the disk. When the first bank has finished collecting data, the roles of these two banks are switched, ensuring that all data generated are collected.

Microprocessors on a VME rack are used to handle data transfer from the ECL circuitry to a Priam SD107 300 Mbyte hard disk, as well as operator interaction with the ITR. The step which currently limits the mass spectral production frequency is the process of writing to the disk. Transferring information from 5000 time windows to the disk limits the maximum scan file production rate to 25 summed spectra per second. Through the use of peak finding algorithms on parallel processors, the quantity of data written to the disk is reduced, increasing the maximum scan file generation rate to 60 summed spectra per second. The operator has control over the number of scans summed and therefore, the scan file generation rate. In addition, the operator can adjust the instrument trigger frequency and hence cover large mass ranges when needed.

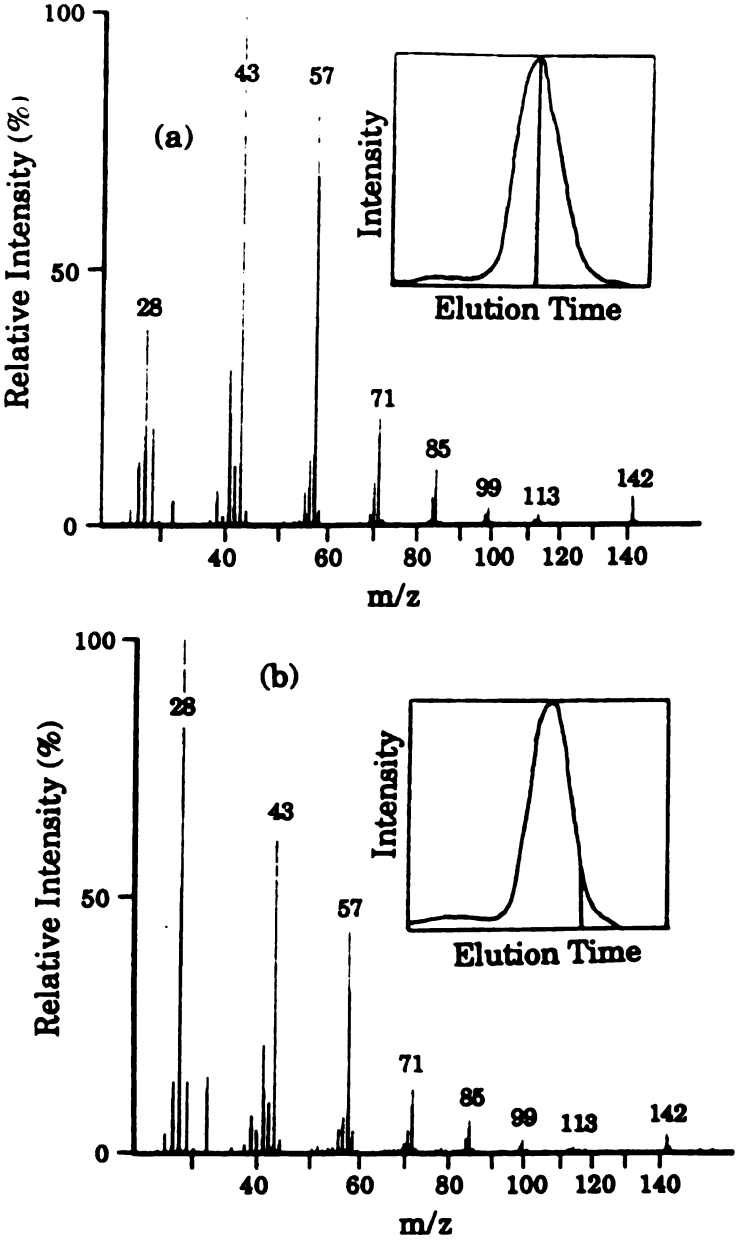
Results and Discussion

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. Two features of data collection can influence this quality. The first involves ion counting statistics, while the second occurs from changes in source concentrations during acquisition of the mass spectrum.

The mass spectrum is derived from concentrations of ions in the source upon the application of the ion extraction potentials. Formation of ions in the source is a function of the instantaneous concentration of molecules in the source. Ion formation occurs over 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 confined to the potential well formed by the electron beam [4]. The ion concentrations in the source upon the initiation of ion extraction are therefore an integration of all instantaneous ion concentrations during the ion formation process. During the time required to extract ions from the source, ion concentrations do not change perceptably. 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 mass spectra collected by the TAD process from any point on a chromatographic elution profile are identical within the limits of noise. This is illustrated by data in Figure 3.4 in which the spectrum of n-decane is shown as acquired at the apex (Figures 3.4a) and at the side of the elution profile (Figure 3.4b) at a scan file generation rate of 10 scans per second (1000 summed transients). An air background can be observed in these figures at 28 and 32 Daltons. Except for this air contaminant, mass spectral intensities in these two figures agree within ±3%. Much of the error can be attributed to the increase in the background interference in the spectrum collected on the side of the elution profile, caused by the lower partial pressure of n-decane in the source.

The consistency of 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 ratio of peak intensities at m/z



3.4. The mass spectrum of n-decane collected at (a) the top and (b) on the side of the chromatographic elution profile. Spectra were collected by summing 1000 transients.

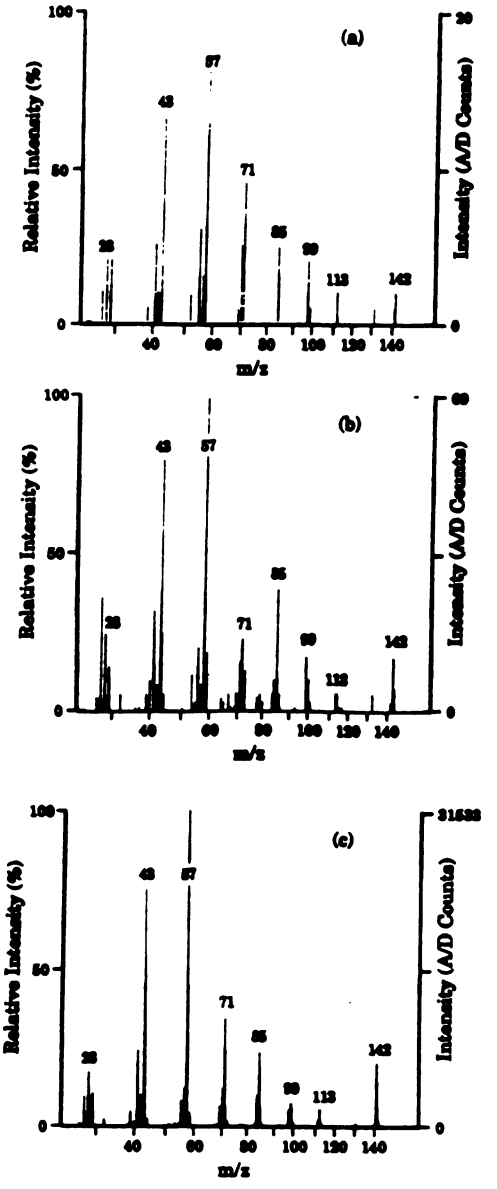
29, 71, and 142 relative to that at m/z 43 was determined in each of 14 consecutive summed spectra (1000 transients summed) collected across the chromatographic elution profile of n-decane. The ratio of these peaks was also determined in each of 14 consecutive summed spectra obtained from n-decane at a constant source pressure. These ratios are presented in Table 3.2. 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 S/N as the partial pressure is decreased. Mean relative intensities from these two tests were within 1% of each other.

Table 3.2. Percent ion intensities relative to m/z 43 for successive scan files of n-decane under dynamic and steady-state conditions.

	Steady-State Intensity			Chromatographic Intensity		
	29	71	142	29	71	142
	18.61	19.62	5.15	19.53	20.71	5.74
	17.83	20.47	5.62	17.92	20.37	5.88
	18.60	21.40	5.06	17.53	19.30	5.30
	18.76	19.19	5.14	19.07	21.86	5.71
	18.88	19.65	4.57	19.12	20.42	5.27
	17.56	19.01	5.13	18.56	18.67	5.12
	17.03	21.58	4.94	19.86	19.38	5.19
	17.65	20.18	4.98	20.03	18.17	5.31
	19.21	21.33	4.80	18.19	19.59	4.67
	18.25	19.46	5.44	17.88	17.48	5.88
	18.29	19.96	5.29	18.26	19.58	4.49
	18.85	19.74	5.22	17.81	18.42	5.22
	20.03	20.41	5.14	17.48	20.86	5.84
	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%

Spectra in Fig. 3.5 were obtained by summing different numbers of transients while the pressure of n-decane in the source was held at $5x10^{-6}$ torr. These spectra illustrate the improvement in precision obtained by summing additional successive transients. Quantization noise is apparent in the spectrum from a single transient (Fig. 3.5a). This spectrum contains many of the features of the reference n-decane spectrum, but there are deviations in relative peak intensities due to the low overall signals; in fact, at low analyte concentrations, a signal at a given m/z value may be missing in any given individual transient. For example, peaks at m/z 29, 53, 99, and 127 are more intense than they should be, while peaks at m/z 32, 83, 84, and 98 are missing entirely from this spectrum, obtained from a single transient. With as few as 10 transients summed (Fig. 2b), the spectrum is noisy and not all relative intensities are consistent with the reference spectrum, but it has all peaks in the reference spectrum are present. This spectrum corresponds to a scan file generation frequency of 1000 Hz. In summing 10,000 transients (Fig. 2c), features of the spectrum are not significantly altered but a clean spectrum with a very high signal-to-noise ratio is obtained.

The improvement in signal-to-noise ratio 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 ratio was performed by collecting fifty repetitive spectra of n-decane at different numbers of summed transients. The signal intensity was determined for several values of m/z. The noise was determined as the variance in the signal intensity. Results from these experiments are presented in Figure 3.6. While the value of S/N increases significantly with the number of transients summed, it does not follow the predicted square root relationship. This non-ideality stems from the fact that the prototype version of the ITR produces a non-random noise



3.5. The mass spectra of n-decane collected by summing (a) 1, (b) 10, and (c) 10,000 transient spectra. This corresponds to scan file generation frequencies of 10000, 1000, and 1 Hz respectively.

component of the signal that is synchronized to the sampling of the A/D converter. This component of the noise, like the signal, is enhanced with each summing. The signal-to-noise ratio can be expressed algebraically as:

$$S/N = A\,(n)^{0.5} \;/\; (B + C\,(n)^{0.5} \qquad (3.1)$$

where A is the proprotionality constant for the signal, B is the proportionality constant for the random component of the noise, C is the proportionality constant for the non-random component of the noise, and n is the number of transients summed. At low numbers of summed transients, white noise is the major contributor to the noise in the signal. As the number of transients are increased, the random contribution increases as a factor of the square root of the number of transients summed while the synchronous contribution increases proportional 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 ratio becomes constant. Hence, summing more than 2000 transients with the current version of the ITR does not provide any advantage in the signal-to-noise ratio. This can be observed in Figure 3.6 as the leveling off of the curve at large numbers of transients summed.

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 (5). The multiplex advantage states that an increase in the S/N ratio 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

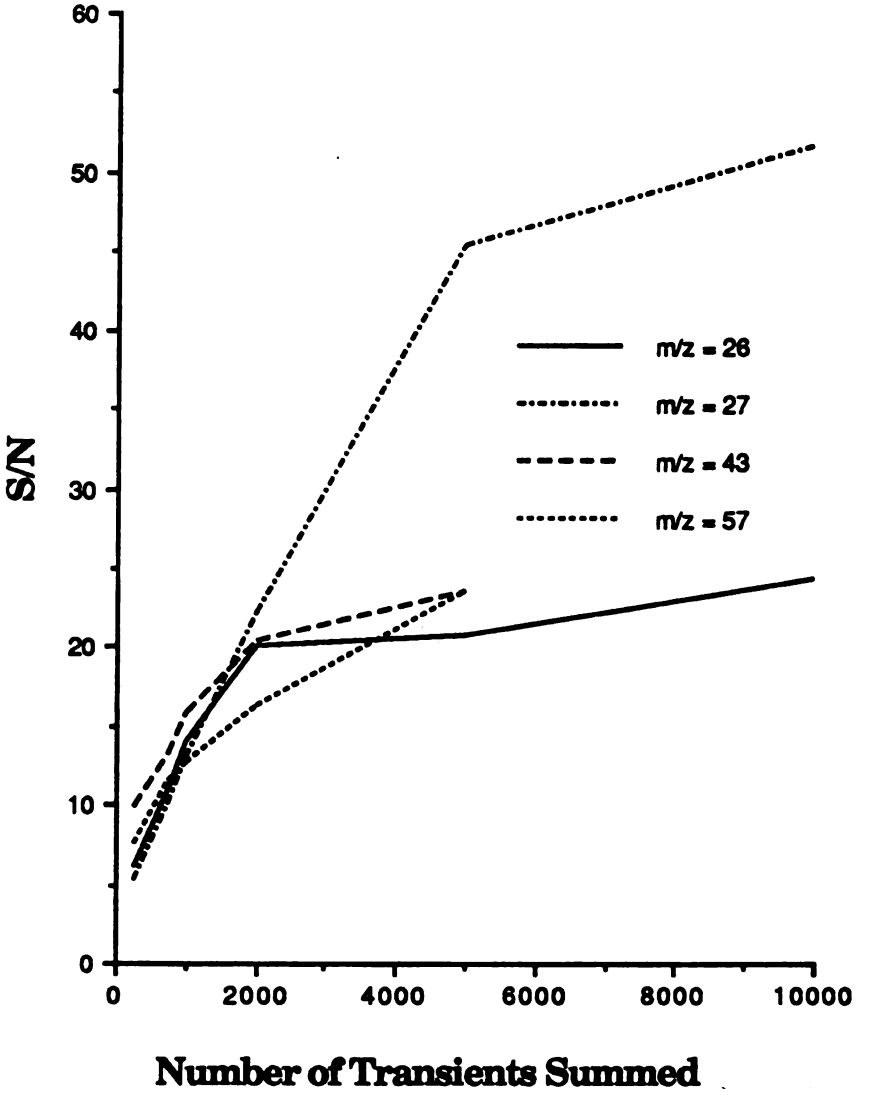


Figure 3.6. The relationship between S/N and the number of transients summed.

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 20 to 160 Daltons would provide a S/N improvement of a factor of 71 over TOFMS instruments which use a boxcar integrator with a 5-ns window to scan the spectrum. Assuming that readout noise can be neglected, the 16,000 time-bins used in TAD would provide a S/N improvement of a factor of 126 over scanning TOFMS instruments which use a 5 ns window.

Mass Spectral Calibration

The capacity to collect spectra that are the linear sums of unskewed transient spectra opens new avenues for data reduction algorithms. It is now possible to subtract the contribution of one spectrum from another when overlapping chromatographic peaks are encountered, without having to account for skewed spectra caused by differences between steady-state and dynamic spectra.

Interpretation of a mass spectrum includes the assignment of m/z values to mass spectra. Output from the ITR lists ions by their flight times rather than m/z values. It was necessary to write a program which could be used to reduce ITR data to mass-intensity pairs. The program CVCMASS was written in FORTRAN on a PDP-11/43 and later on a MICROVAX-2 to perform this function. A listing of this program is included as appendix II of this document. This program was developed from the following linear relationship:

$$t_{of} = k\,(m)^{0.5} + C \qquad (3.2)$$

where t_{of} is the ion flight time to the detector, m is the ion's m/z ratio, k is a collection of constants, and C is an offset constant. CVCMASS can be used to calculate the calibration parameters from data in a run file, or just to transform the data to mass/intensity pairs using predetermined values of the calibration parameters.

In the process of calculating the calibration parameters, CVCMASS requires the input of three approximate flight times for known m/z values. The program then searches the source file for all occurrences of these flight times, within 30 ns windows, to determine the mean values of flight time for each of these ions. Ion intensities below a threshold of 50 are ignored to minimize noise. Values of k and C are then calculated from the solution of simultaneous equations. Mean and standard deviation determinations are made for each of these parameters and reported to the terminal. If the standard deviation of either value is too large, an error was made in the initial assignment of the m/z value. Shifting values of k over a period of time are indicative of changing conditions in the source, such as contaminated grids or unstable voltages. Shifting values of C are indicative of changes in the pulsing of the source and can originate from either the trigger pulse on the ITR, or one of the pulsing boards on the CVC 2000.

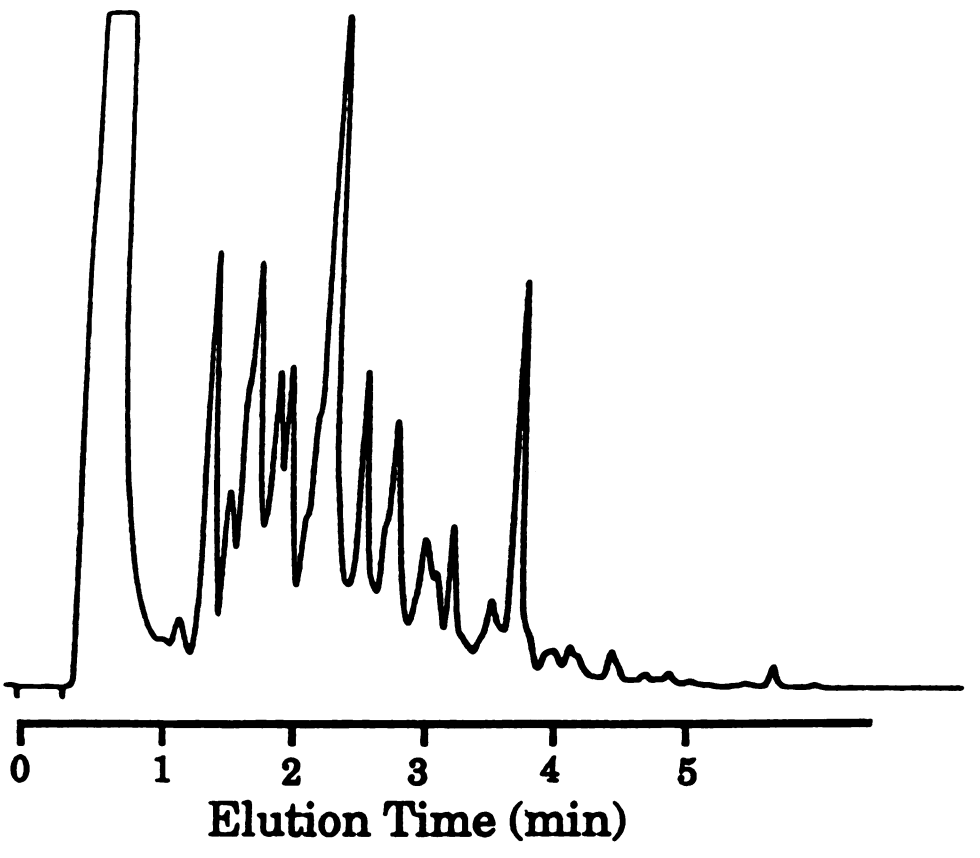
Once the calibration parameters have been determined, CVCMASS uses these parameters to convert the flight times in the source file to m/z values and writes the data to the destination file in a format that can be read by other data reduction programs written during this research. While working on this program, it was noticed that at random intervals mass assignments of peaks in the mass spectra were too low and flight times for

these erroneous assignments were always multiples of 80 ns low. Once a shift occurred in a mass spectrum, all peaks at higher m/z values in that spectrum were also shifted. CVCMASS was modified to print a warning message when peaks were outside of a 0.3 Dalton window centered at integer values. Using this feature of the program it was determined that this shift occurs randomly in 2 to 18 percent of the spectra collected. No correlation was observed between the rate at which data were written to the disk and the probability of a shift in the flight time. The problem is most severe when large mass ranges are stored to the disk. The source of this problem appears to arise from a counter in the ITR which is used to locate the next time bin to read out to the disk. It appears that this counter is being incremented randomly. Attempts to observe an extraneous incrementing pulse have thus far been fruitless.

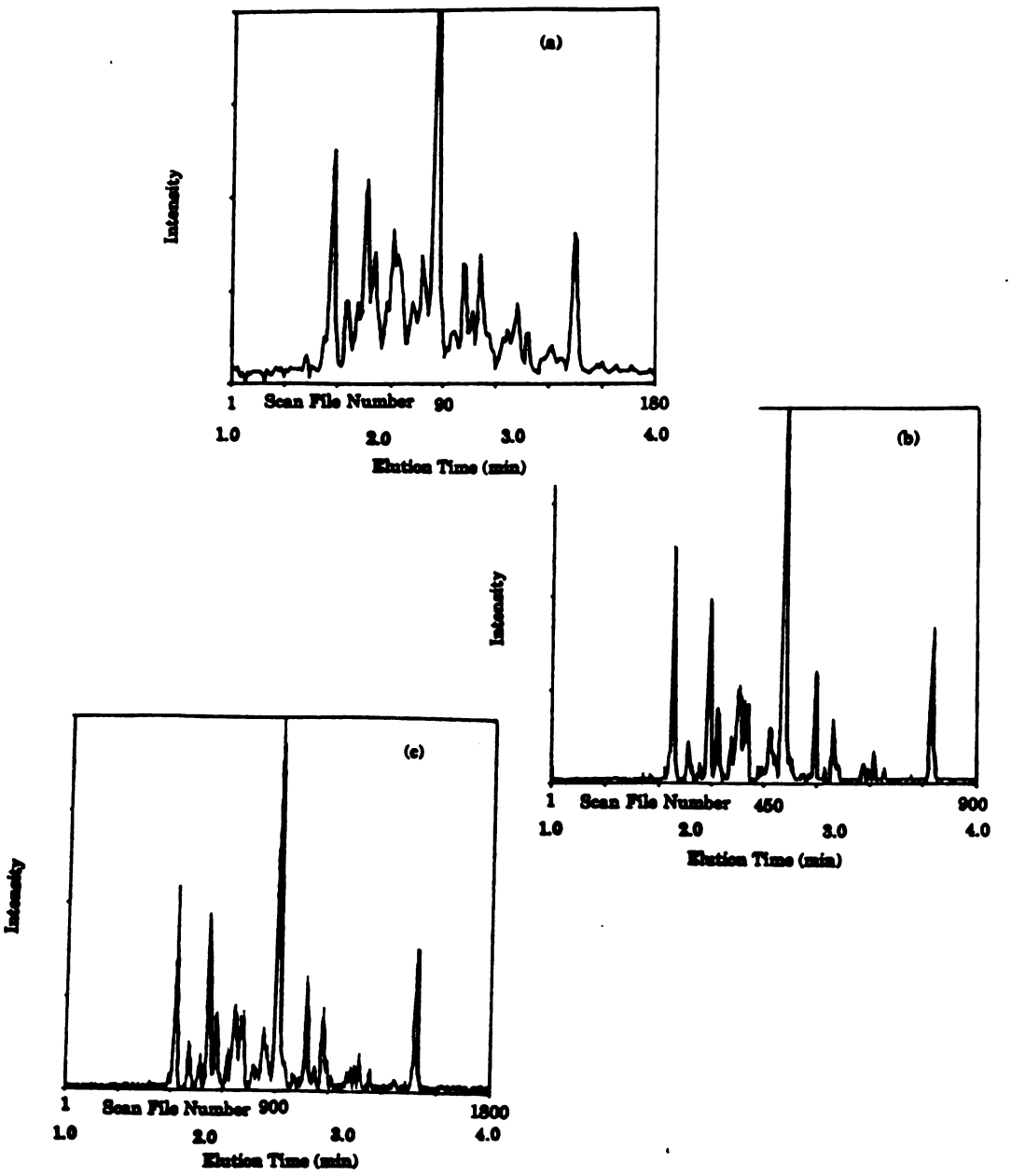
Representation of the Chromatography.

Information desired from a GC-MS analysis is usually centered around the identification of chromatographic eluents. A reconstructed chromatographic profile can be used to locate the best spectra to represent 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 samples be collected for each chromatographic peak (6) depending on the degree of accuracy desired.

The capacity to accurately reproduce the chromatographic profile from a limited number of mass spectra is illustrated in Figures 3.7 and 3.8. These figures were collected using different gas chromatographs under similar chromatographic conditions. The FID chromatogram of a charcoal lighter fluid is shown in Figure 3.7 and represents the analog chromatogram, unrestricted by the bandpass of the data collection system. The time-array detection system permits the selection of sampling frequency by providing control over the number of transients to sum. Reconstructed chromatograms were obtained from separate injections of charcoal lighter fluid with different numbers of transients summed per scan file. These reconstructed chromatograms are included as Figure 3.8. Differences between Figs. 3.7 and 3.8 are due in part to the non-specificity of the flame ionization detector (Fig. 3.7) while mass spectrometers are a little more specific. In addition, subtle differences in the chromatographic conditions between the two instruments can alter the chromatographic separation process. Chromatographic peak widths range from 3 to 4 seconds at baseline. The apparent chromatographic resolution increases as the sampling frequency increases from 1 to 5 to 10 Hz (3 to 15 to 30 samples across the peak profile). Relative chromatographic peak heights do not significantly change when mass spectral generation frequencies above 5 Hz are used. In addition, the signal level in the reproduced chromatogram decreases as the mass spectral generation frequency is decreased, which causes an associated decrease in the S/N ratio. For each different chromatographic condition, 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.



3.7. An FID chromatogram of charcoal lighter fluid injected onto a 22 m by 0.25 mm fused silica capillary column coated with 0.25 μm SE-54. The GC was temperature programmed from 100°C to 150°C at 10°C/min.



3.8. Reconstructed chromatograms of lighter fluid from scan file generation frequencies of (a) 1 Hz and (b) 5 Hz. The GC was temperature programmed from 100°C to 150°C at 10°C/min.

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) m/z values is monitored. Of course, when SIM is used, information about ion current at all other m/z values is sacrificed. Because time array detection permits the collection of complete mass spectra, all mass spectral information generated is retained. The ITR integrates the ion current in each 5-ns time window from successive transients in much the same way as do conventional TOFMS instruments when the boxcar integrator is not scanned (SIM mode), thus, detection limits for complete spectra obtained by TAD should be the same as those otherwise achievable in TOFMS only by SIM.

The method of chromatographic reconstruction used in this work differs from that used in conventional total ion chromatograms. Conventionally, the sum of all ion intensities in each scan is used to create a single point on the reconstructed chromatogram. The algorithm used in this work saves time in the data reduction by plotting the difference between the highest and the lowest values in each scan file. The resulting "DIFFerence plot" is still useful in locating the desired scans, but relative peak intensities are not as analytically useful as in the conventional technique.

In order for TAD to become a viable detection method for GC-MS, detection limits by TAD need to be comparable to those found using other mass spectrometers. This could be a problem using the CVC 2000 since a pulsed source is used in which ions are only formed for 1 to 4 μs out of the 100 μs duty cycle. In addition, ions are only extracted out of the source once every duty cycle. This is in contrast to mass spectrometers with continuous ionization and extraction and will result in a decrease in signal intensity.

To increase the sensitivity of TOFMS, the electron control slit was grounded permitting continuous ionization in the CVC 2000 source. This experiment should have increased the number of ions in the extraction packet since ions are trapped in the electron beam [4]. The response at the detector should increase by as much as a factor of 20. In addition, the effect of metastable decompositions after ions leave the source should be reduced since decompositions and ion-molecule collisions are likely to occur while the ions are being stored [7]. Signal intensities were determined to be a factor of 4 higher than found using a 4 μs ionization time. This indicates that some ion storage did occur, but also that ions were able to leave the extraction volume prior to application of the extraction pulse.

Serial dilutions of toluene in hexane were used to determine detection limits while using continuous ionization. A "DIFFerence plot" of an 11 ng GC injection of toluene is included as Figure 3.9. At a S/N 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 2 scan files per second. Operation of the TAD system at the same scan file generation frequency as the quadrupole instrument is performed by increasing the number of transients summed, and hence, would result in lower detection limits by TAD for similar sample generation frequencies. In addition, the sensitivity of quadrupole instruments has improved over many years of instrument evolution, while comparitively little work has been done on pulsed TOFMS sources towards such optimization. The sample-use duty cycle of the pulsed TOFMS source is often so low that the detection limits achieved are worse than those of continuous beam mass filter mass spectrometers. One way to improve the signal-use duty cycle is to store ions created between extraction

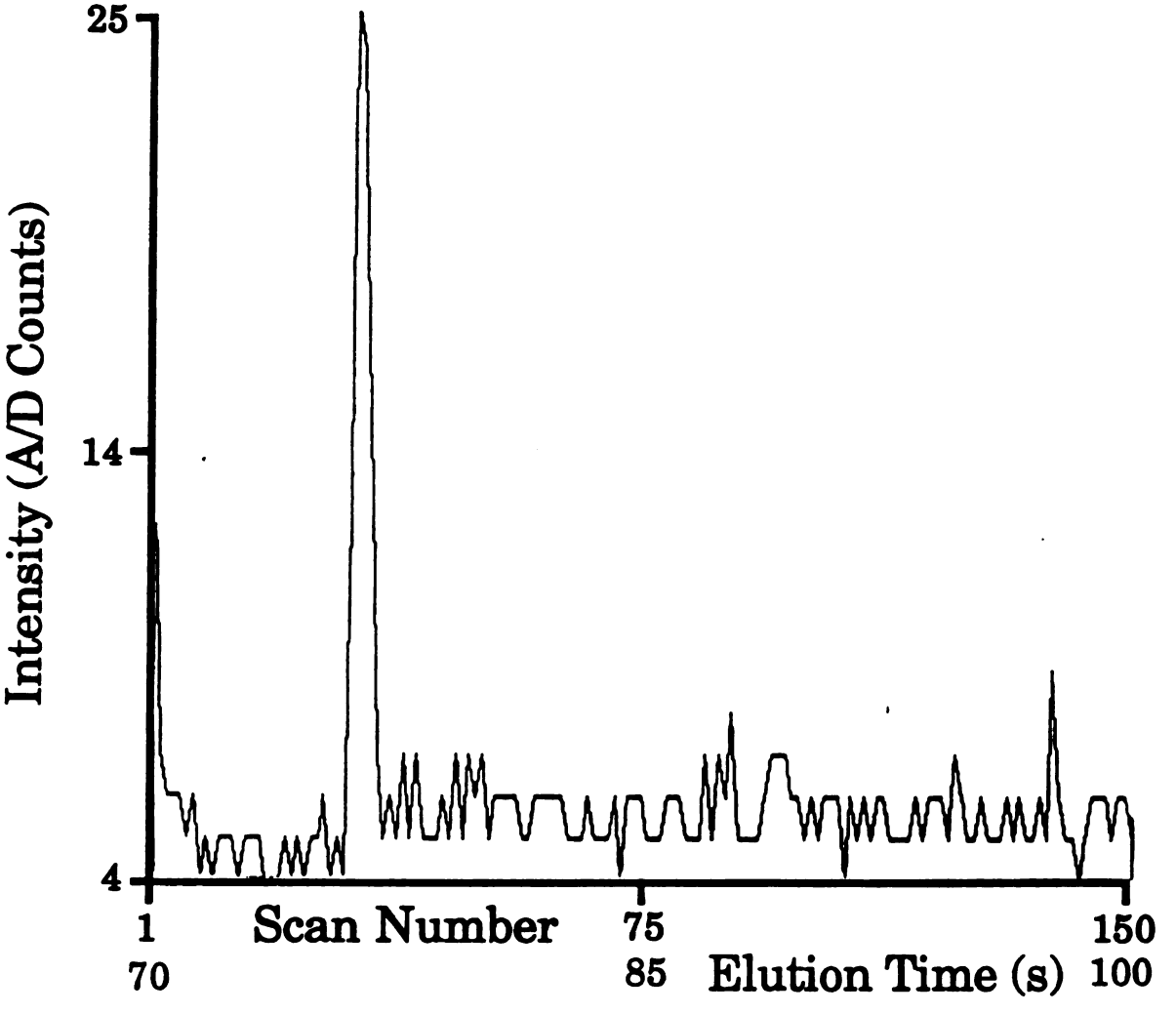


Figure 3.9. Reconstructed chromatogram of 11 ng injection of toluene collected at a scan file generation frequency of 5 Hz.

pulses. This initial attempt resulted in a four-fold improvement in sensitivity over pulsed ionization. Further work should produce still better results, potentially to much better levels than exhibited by scanning filter mass spectrometers. Note that since Figure 3.9 is a DIFFerence plot the intensity is that for the most intense peak in the spectrum, m/z 91, not the total ion intensity, so information from the rest of the spectrum is still available. TAD offers the option to search the data for just the m/z 91 peak in the spectrum of toluene, reducing the background noise and lowering the detection limit. Scanning instruments suffer from insufficient sampling frequencies when using this quantitation method, but such a problem does not exist with TAD since data collected represent rapid changes in source concentrations.

Speed of Analysis.

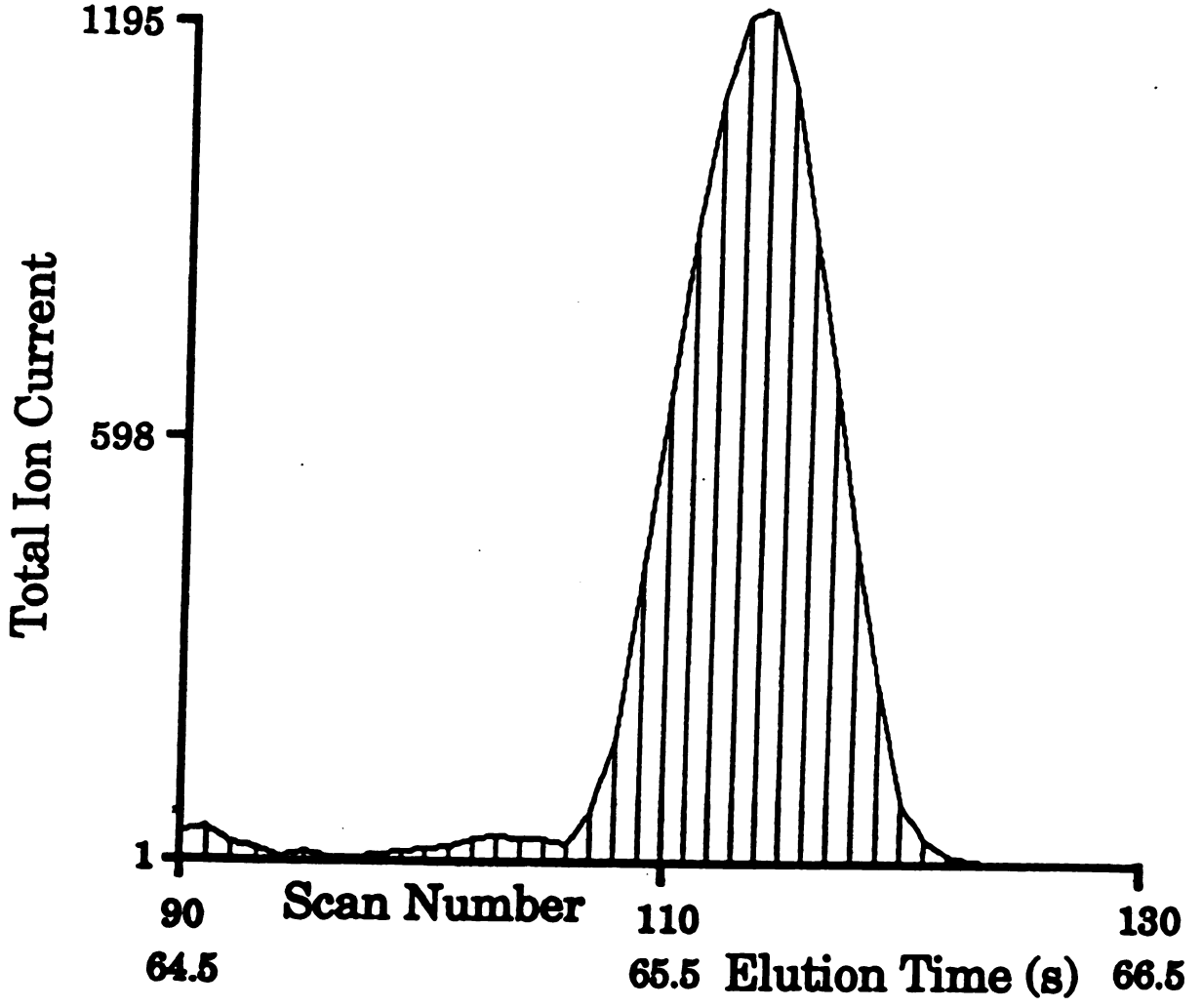
When the scan file generation rate is not a limiting factor, the chromatography can be optimized for speed of analysis, greatly reducing the time needed to perform an analysis. The shorter analysis time results in a corresponding increase in the chromatographic peak heights, compensating for the loss in S/N from the requisite higher scan file generation frequencies. Typical GC-MS analysis times for these types of mixtures are on the order of 12 to 60 minutes (8). 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 Fig. 3.8 were collected from a charcoal lighter fluid sample in less than 4 minutes. 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 have been obtained under similar conditions through the trimethylbenzenes in less than 2 minutes. While these

conditions are not advisable for the separation of small hydrocarbons, the xylenes and other aromatic isomers are adequately separated. In addition, the use of cold trapping inlets with capacitative heating has been reported to separate nine of the major components in gasoline in as little as 2.5 seconds (9).

An example of the scan file generation rate possible with TOFMS-TAD is illustrated in Fig. 3.10, which is a segment of a reconstructed total ion chromatogram representing the analysis of gasoline by capillary column GC-MS. The major peak in Fig. 3.10 is due to 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 readilly recognizable as toluene mass spectra. This peak is only 0.7 seconds wide at baseline. 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. Additionally, mass spectrometry offers the possibility of deconvoluting overlapping chromatographic peaks when there are unique ions in the spectrum of the individual components (10). Inconsistent mass spectra, as in 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 unskewed mass spectra across the entire chromatographic elution profile, better success in the application of deconvolution and pattern recognition algorithms can now be expected.



3.10. Reconstructed chromatogram of the toluene peak in unleaded gasolene. Spectra were collected at 20 Hz. The collection of each spectrum is represented by the vertical bars.

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CHAPTER 4:
RECONSTRUCTED CHROMATOGRAMS BASED ON MASS SPECTRAL DEGREE-OF-FRAGMENTATION

INTRODUCTION

Time-array detection permits an accurate reproduction of the chromatographic elution profile, but only when high scan file generation frequencies are used. However, these high frequencies result in large numbers of mass spectral data files for interpretation. For example, a 1hr gas chromatographic separation sampled at a frequency of 20 Hz results in the production of 72,000 mass spectra; only a limited number of these contain information that is analytically useful. The time needed to interpret these spectra could be reduced through the use of computer algorithms which filter data based on a common characteristic of the species of interest prior to interpretation. In this manner, only spectra of interest for the analysis at hand will be flagged. All collected data are retained in case they are needed for other purposes.

The most commonly used prefiltration algorithm involves the production of a reconstructed total ion chromatogram[1]. This algorithm involves passing the sum of all ion intensities in the spectrum to the plot file. In this manner, a non-selective response is obtained for each

chromatographic eluent. If the entire mass range is collected, if the electron cross sections of all neutral molecules is identical, and if all ions produce identical gains at the multiplier, this algorithm will generate chromatograms in which the molar response for one compound, as indicated by the intensity of its chromatographic peak, can be used to quantitate all other components based on their corresponding peak intensities. When these conditions are approximately valid, relative peak intensities can still provide a rough quantitation of chromatographic eluents.

The prefiltration algorithm used on the ITR, DIFFerence plots, involves passing the difference between the most and least intense points in the spectrum to the plot file. This algorithm responds to all chromatographic eluents, but in a manner that is a function of the eluent concentration and the number of peaks in the spectrum. This method enables the rapid location of eluent spectra in the data base, but sacrifices quantitative information in the reconstructed chromatogram.

It is often beneficial to obtain more specificity than can be obtained from either of these algorithms in order to further reduce the number of mass spectra that need to be interpreted. The algorithm most commonly used to provide this added specificity involves the production of a reconstructed mass chromatogram [2]. This method involves a search of the data field for a specified m/z value. When such a value is found in a spectrum, the intensity of that m/z value is passed to a chromatographic plot file. If the selected m/z value is not in the mass spectrum, a 0 is passed to the plot file. This algorithm is useful for monitoring classes of compounds with common fragment ions, such as phthalate esters (m/z 149) or alkanes (m/z 43 and 57). Selection of ions for the search can be made from tabulations of structural

correlations [3]. This algorithm is also used to locate spectra of chromatographic eluents with a particular molecular weight by monitoring the ion current at the m/z value that correlates to the desired molecular ion.

Now that some tandem mass spectrometric methods can be performed on the time scale of capillary chromatography [4], an alternative selective filtration method is becoming feasible which is based more on ion chemistry than on ion mass. The GC-MS/MS data space can be searched for characteristic m/z ion daughters or losses. Intensities of qualifying ions can then be passed to the chromatographic plot file. In this way, chlorinated hydrocarbons could be identified by their characteristic losses of m/z 36 (HCl) or m/z 70 (Cl_2). These filtration methods provide an advantage over reconstructed mass chromatograms in that they bestow additional chemical information about eluting species. However, they require specialized instrumentation as well as advance information about the sample matrix.

Situations often arise in which few common features are available in the mass spectra of chemically related compounds. Examples include the analysis of aromatics [5] and polyaromatics [6,7] where the electron impact mass spectra are sparsely populated and the limited features that are present have few structural associations. One feature these spectra do have in common is their paucity of peaks, a direct result of the strength of resonant bonds in aromatic species [8].

The lack of common spectral features in mass spectra of highly aromatic species limits the usefulness of either of the two previously mentioned specific filtration algorithms. A desire has been expressed for analytical methods which amplify signals from these structures while eliminating signals that interfere with their detection [4]. An example of

where these methods are needed is in the analysis of combustion residues where aromatic species make the largest contribution to the toxicity [5,6] or can be used to identify the accelerant used to initiate combustion [7,9]. In each of these cases, only a few of the hundreds of chromatographic peaks represent aromatic constituents of the sample matrix. It could prove beneficial for these applications to use an algorithm which examines mass spectral data based on the profusion of peaks and their distribution in each spectrum. Such a selective filter would permit mass-independent discrimination of species that have a large number of fragment ions, such as alkanes, from those with only a few fragment ions, such as polycyclic aromatic hydrocarbons (PAH), inorganics, and molecules that easily fragment via a single pathway to a stable ion, such as nitroaliphatics.

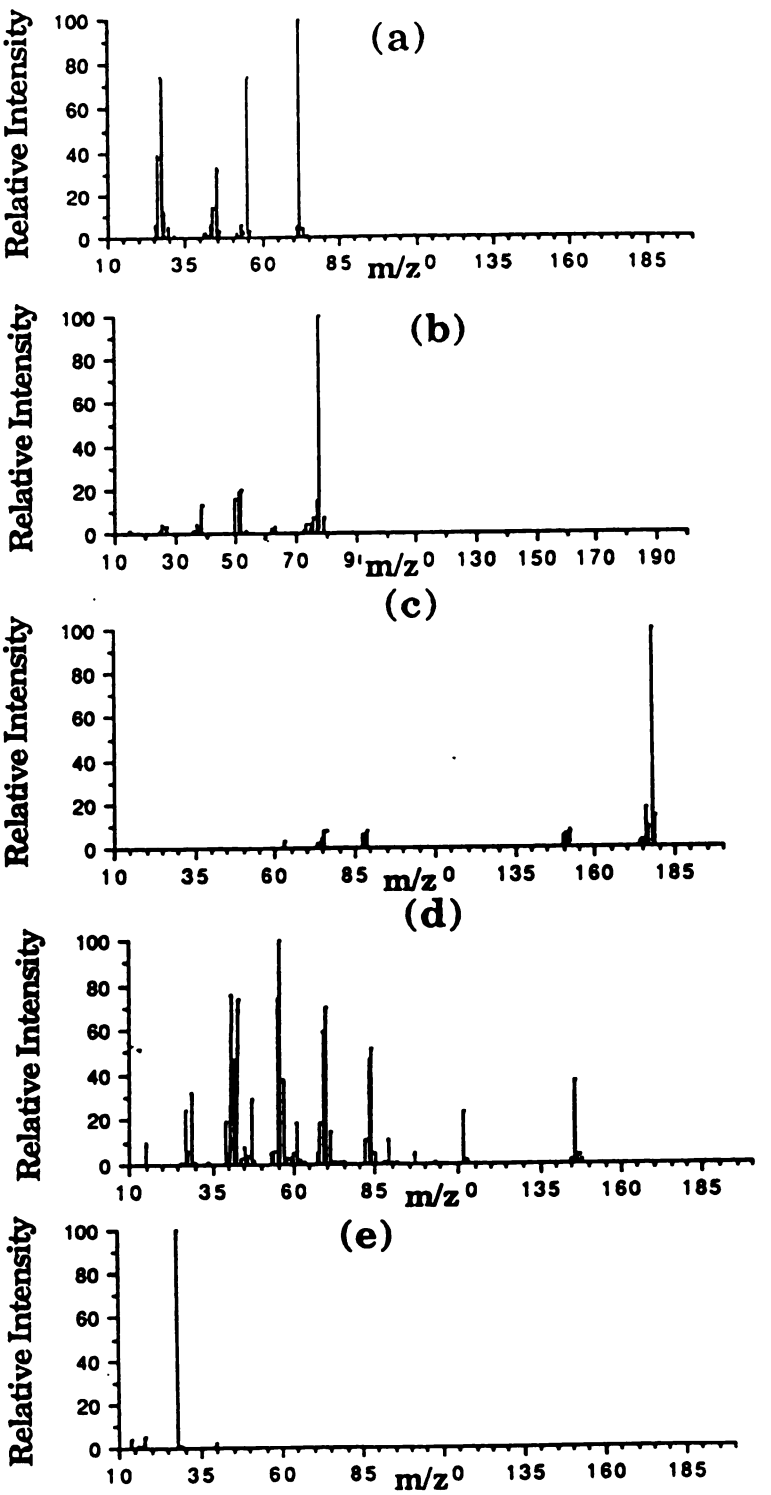
Two algorithms have been examined as part of this effort for use in filtering GC-MS data based on the degree-of-fragmentation of ions. The foundation for the first algorithm is the fact that highly aromatic compounds have most of their mass spectral intensity confined to only a few peaks. The second algorithm is based on the number of peaks in the spectrum, which is low for aromatic compounds [10] and high for aliphatics.

Experimental

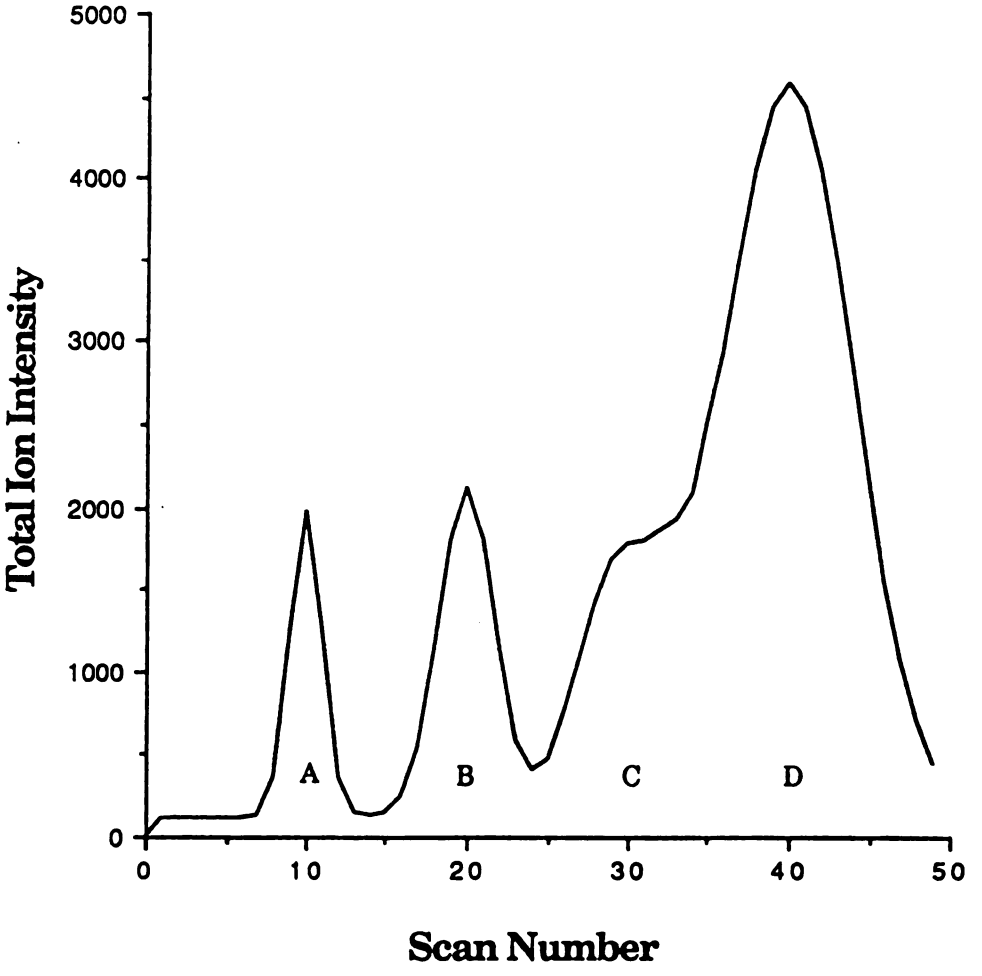
Algorithms written to generate reconstructed chromatograms are included in the program GCSIM.C in Appendix III. This program was written in C on a MicroVAX II. It takes output from CVCMASS.FOR (Appendix II) and creates a data plot file for reconstructed TII, DIFF, mass, and degree-of-fragmentation chromatograms. The resultant data plot file is compatible with CricketGraph [11].

A data set was created from normal (Gaussian) distributions of five different mass spectra, representative of a GC-MS data field, to test the filtration algorithms. Mass spectra chosen are presented in Figure 4.1. Benzene and anthracene (Figures 4.1b and 4.1c, respectively) were chosen as representative of aromatic eluents. Spectra of acrylic acid and octylmercaptan (Figures 4.1a and 4.1d, respectively) were selected as representative of spectra with much fragmentation. Fifty successive spectra (scans) were created using evenly spaced distributions of varying amplitudes and variances from the mass spectra of these four compounds to simulate data from a GC-MS analysis. Variances for individual spectra were selected to produce two separated and two unseparated peak shapes, as shown in the TII reconstructed chromatogram (Figure 4.2). In addition, an air contaminant (Figure 4.1e) was introduced throughout the data set to simulate a high background by selecting a large variance for the distribution of this spectrum.

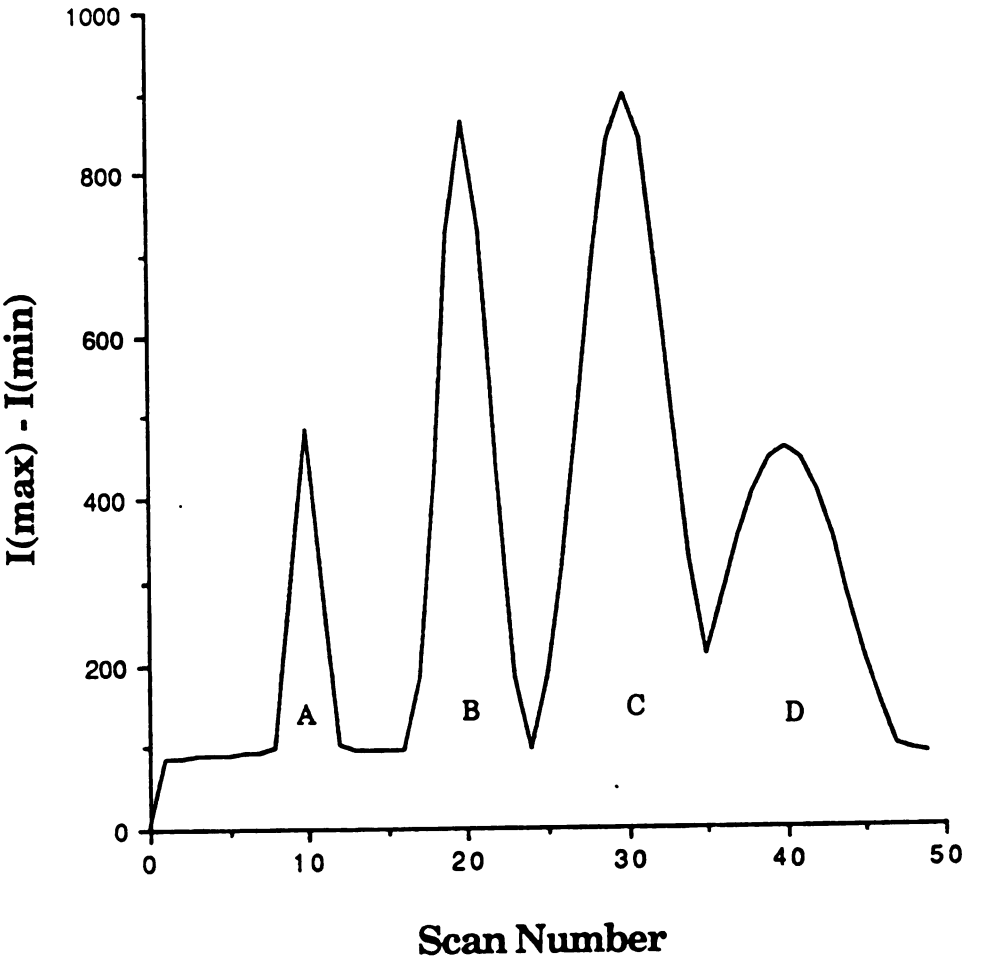
The dependence of the DIFFerence plot algorithm on the number of peaks in the spectrum is illustrated in Figure 4.3. Signal intensity is reduced relative to the TII plot (Figure 4.2) because fewer m/z intensities contribute to the filtered signal intensity. Responses of acrylic acid (A) and octylmercaptan (D) are attenuated relative to those of benzene (B) and anthracene (C). This is a consequence of the fact that the peak intensity in the attenuated species is distributed among many mass spectral peaks, while in the aromatic compounds it is distributed among only a few peaks. The reconstructed TII chromatogram (Figure 4.2) produces peaks whose area is approximately proportional to concentration. The DIFF reconstructed chromatogram contains peaks whose intensity is proportional to the concentration of the eluent, the number of peaks in the mass spectrum, and



4.1. Mass spectra used in the data set for testing degree-of-fragmentation algorithms. Spectra include (a) acrylic acid, (b) benzene, (c) anthracene, (d) octylmercaptan, and (e) air.



4.2. Total ion intensity reconstructed chromatogram of the test data set. Chromatographic peaks are (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.



4.3. DIFFerence reconstructed chromatogram of the test data set. Chromatographic peaks are the same as listed in Fig. 4.2.

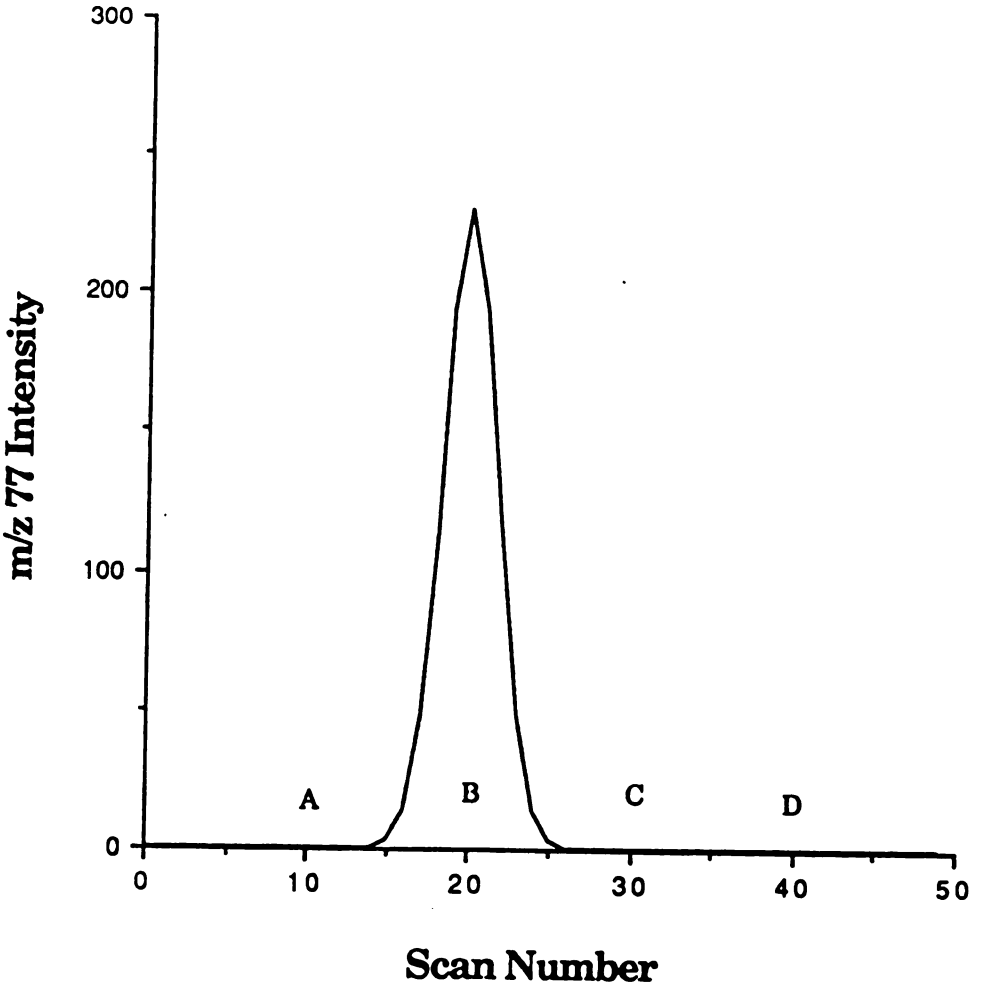
the distribution of intensities among the mass spectral peaks. Quantitative information is not as readily available through the use of this algorithm.

The reconstructed mass chromatogram algorithm was used to search the test data set for monosubstituted phenyl rings (m/z 77). The resulting chromatogram is presented as Figure 4.4. The benzene peak (B) is passed through the filter while all other components are discriminated against. Anthracene has three benzene rings, but there are no common ions between benzene and anthracene that would permit both compounds to pass through this filter.

"Generic Sigma" Algorithm

In much of the older mass spectrometry literature, the percentage of total ionization, %Σ, was used as a measure of the intensity of individual peaks [12]. This value is the ion's peak intensity relative to the sum of all peak intensities above a selected m/z value reported as a percentage. As the sum of all m/z peak intensities approaches the intensity of the peak of interest, the percentage of total ionization approaches 100. When all m/z values in the spectrum are considered, those compounds that produce most of their intensity at only a few m/z values will have high values for percent total ionization at those m/z values while compounds with much fragmentation will have low values for the percent total ionization.

By ratioing the intensity of the most intense peak in the spectrum, the base peak, to the total ion intensity of the spectrum, a value can be obtained that is indicative of the degree-of-fragmentation of the molecular species. This ratio has been designated the "generic sigma" value (Σ_g) because of its similarity to the percent of total ionization axis. In addition to giving



4.4. Reconstructed mass chromatogram of the test data set for m/z 77. Centroids of the chromatographic peaks are labled as in Fig. 4.2.

information concerning the number of different species that can be formed in energetically stabilizing the ion, the generic sigma value would also provide information on the stability of major fragment ions. In this way, some structural information can be obtained.

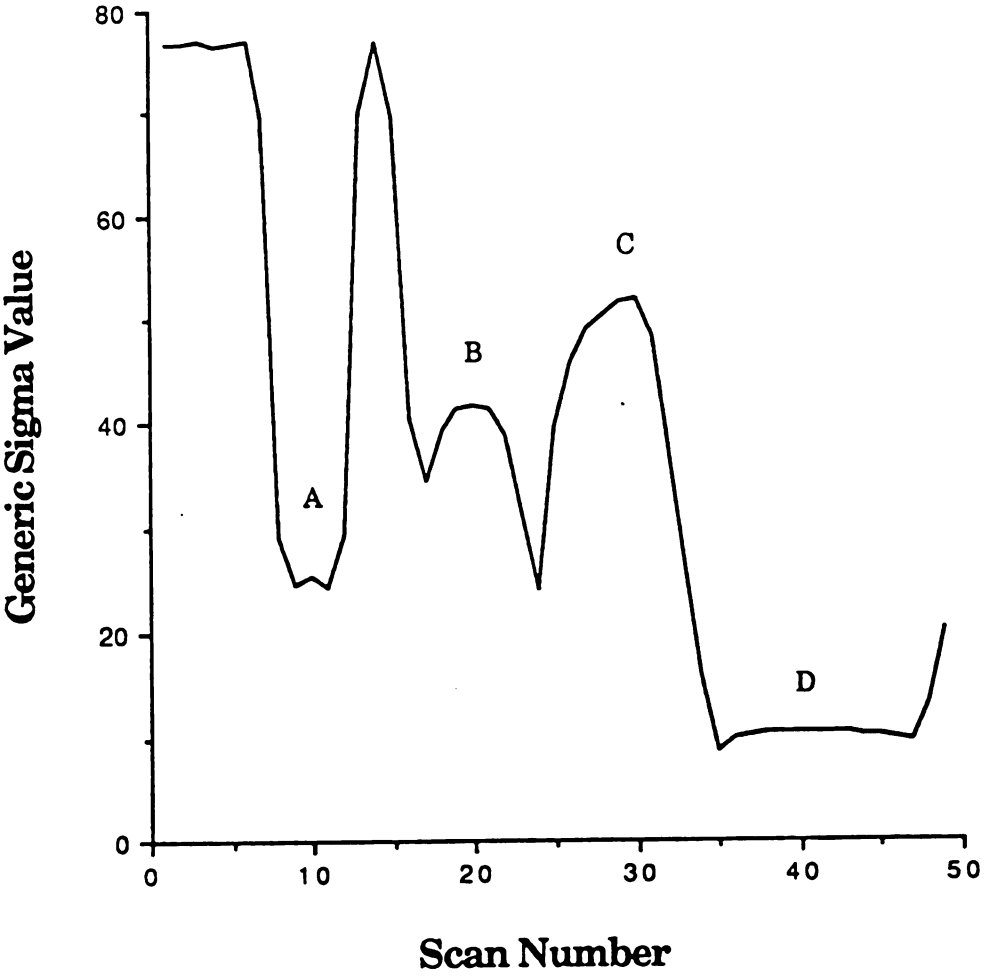
A database of more than 2600 compounds from C_0 to C_{12} has been derived from published spectra in reference 13 in an attempt to demonstrate the utility of the algorithms developed in this chapter. This database is included as Appendix IV. The database includes calculated values of generic sigma (Σ_g) from reference spectra, and is sorted on the number of carbon atoms in the molecule and the generic sigma value. As predicted, species that are highly aromatic have high values of generic sigma while those with largely aliphatic characteristics have low values of generic sigma. Reference spectra used to generate this database were accumulated from a wide variety of mass spectrometers. Work performed by D. Guido [14] has demonstrated that spectral intensities obtained using the cold, open source in the CVC 2000 TOF mass spectrometer differ from spectra obtained using heated, confined sources on other instruments. In addition, the intensity dependence of TOF mass spectra on the time lag that was demonstrated in Chapter 2 of this document can cause a shifting of the generic sigma values in Appendix IV that is dependent on the focus parameters used. These facts limit the utility of this database for TAD data, but the database can still prove useful in determining relative values.

A plot the generic sigma value rather than the total ion intensity against scan number would provide a means of prefiltration which would be independent of the chromatographic intensity. Such an algorithm would be useful in locating both trace and major components in the chromatographic

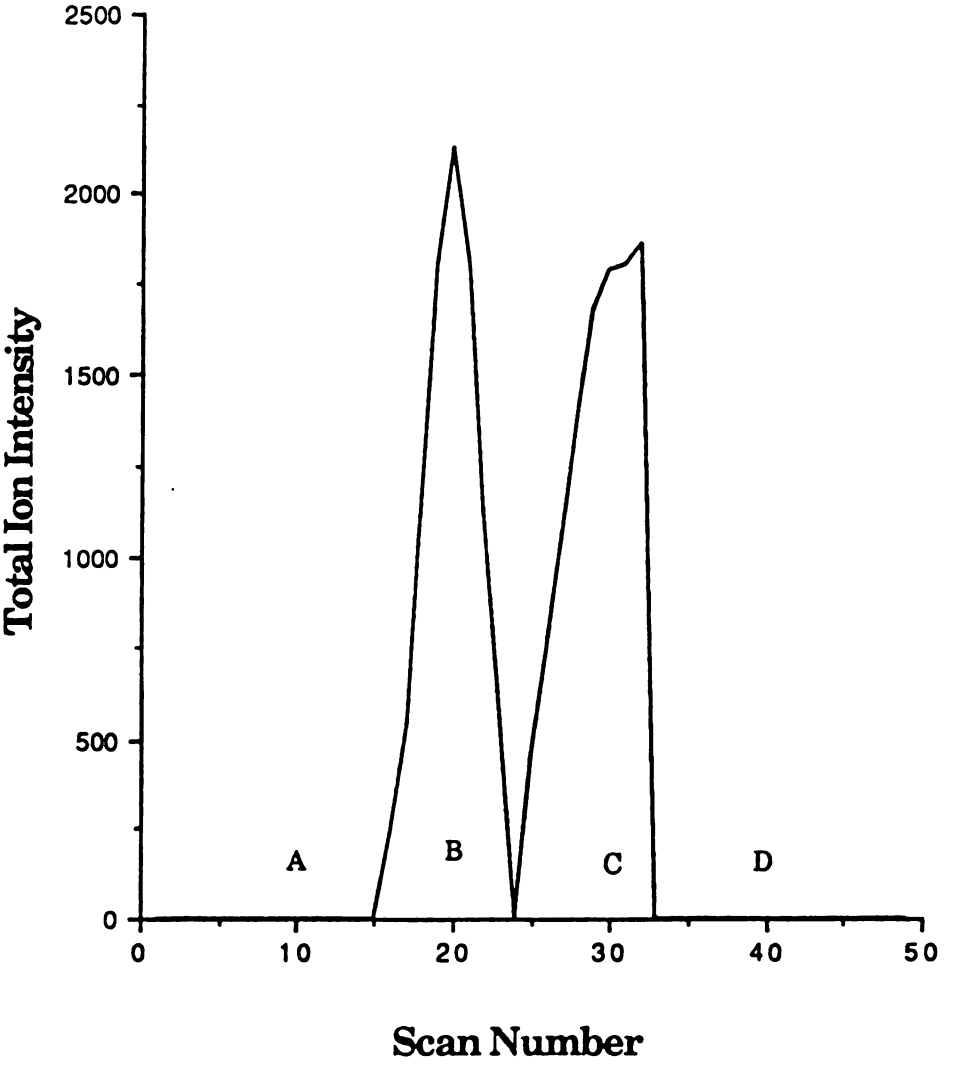
data space, at the expense of any quantitative information. However, when dealing with trace components, it is likely that portions of the spectrum would be of low enough intensity that they would not be recorded. This would increase the value of generic sigma calculated from the GC-MS data file. In addition, a background of air, everpresent in vacuum systems, would result in high values of generic sigma for background and lower values for eluting components.

The generic sigma algorithm was used to produce the reconstructed chromatogram of the test data set in Figure 4.5. Intensities of the base peaks and total ion intensities were determined for each scan file and used to calculate a generic sigma value. Air, which has a high value of generic sigma, is present in the background and causes a high baseline from which depressions indicate the presence of eluents. A broadening of the acrylic acid peak (A) is observed as a result of the gradual increase in the number of peaks as the acrylic acid components grow into the air spectrum. This effect is also responsible for the wings present on the benzene peak (B). The apparent chromatographic resolution is significantly degraded as a result of the overlap of chromatographic components as seen in the response to species B, C, and D.

One means of reducing the contribution to peak broadening from trace contaminants in the mass spectrum is to use threshold values of the generic sigma as a window in which to pass the ion intensity to the plot file, in much the same manner as is done with the reconstructed mass chromatogram algorithm. Figure 4.6 was obtained by passing the total ion intensity to the chromatographic plot file for all scans where the value of generic sigma was between 30 and 60 percent. As with the reconstructed mass chromatogram



4.5. Generic sigma reconstructed chromatogram of the test data set. Centroids of the chromatographic peaks are labled as in Fig. 4.2.



4.6. Total ion intensity reconstructed chromatogram of the test data set in which only compounds in which the generic sigma value is between 30 and 60 percent are plotted. Labels marking the centroids for chromatographic peaks are for (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.

algorithm, values outside of the preselected range resulted in a 0 being passed to the plot file. Under these conditions, the aromatic components are passed to the chromatographic plot file while the aliphatic components are totally discriminated against. The skewed chromatographic peak for anthracene is a result of the overlap with the octylmercaptan peak which results in a decrease in the value of the generic sigma, pushing it outside of the acceptable window.

Problems seen from Figures 4.5 and 4.6 have demonstrated several requirements for the successful use of the generic sigma algorithm. Complete chromatographic separation of the sample matrix needs to be obtained. Mixture spectra from overlapping components will reduce the contribution of the base peak to the total ion intensity, thus lowering the generic sigma value. Because this algorithm is based on intensities, the mass spectral integrity needs to be maintained throughout the chromatographic elution profile or else a wider acceptance range of generic sigma values will have to be used. Such a requirement necessitates the use of TAD. However, the dependence of relative intensities in conventional TOFMS on the focus parameters limits the use of this algorithm to data that have been collected under the same experimental conditions as the spectra used for the data base.

"Number of Peaks" Algorithms

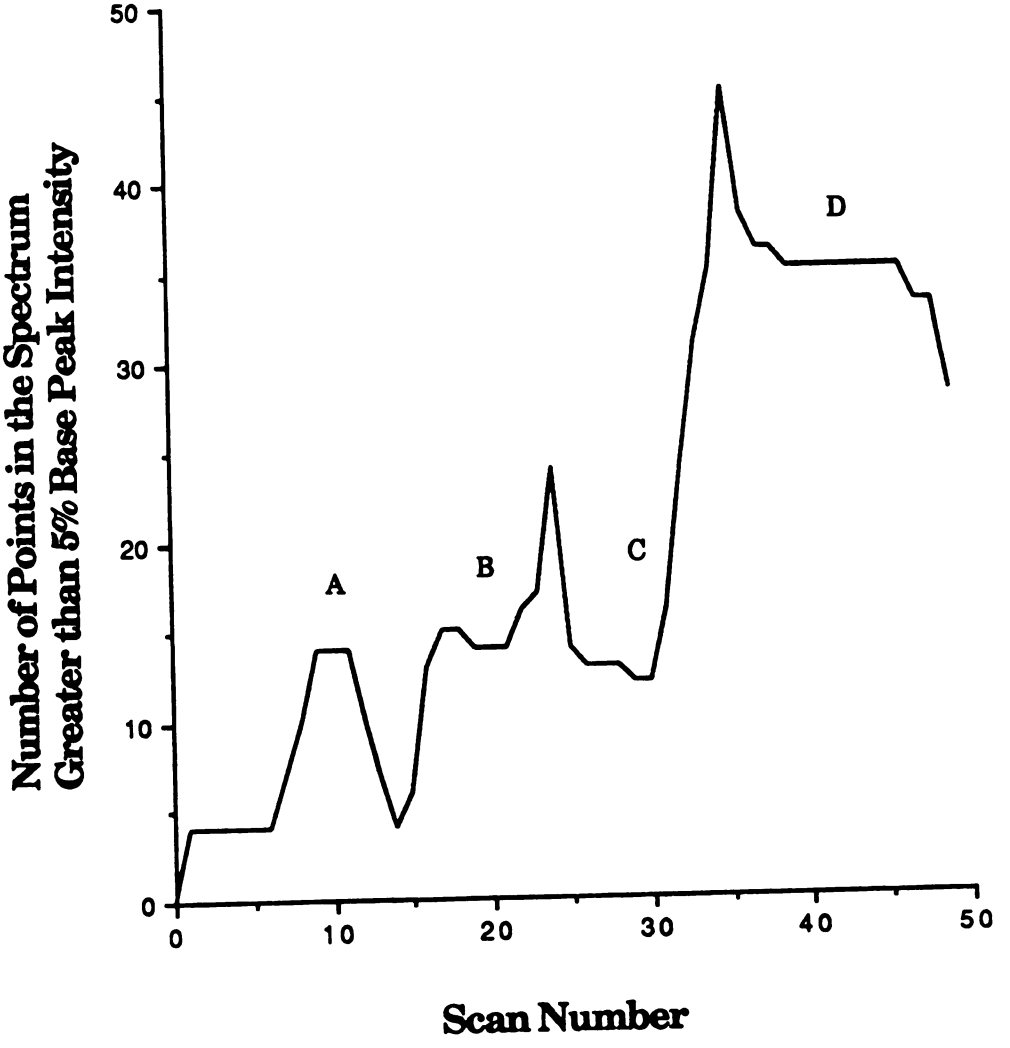
Many of the difficulties with the generic sigma algorithm are due to its dependence on mass spectral intensities. To get around this dependence, a second algorithm was examined which was a function of the number of peaks in the spectrum. Entries have been added to the database in Appendix IV to

incorporate the number of peaks above 5% (NP5) and 25% (NP25) of the base peak intensity.

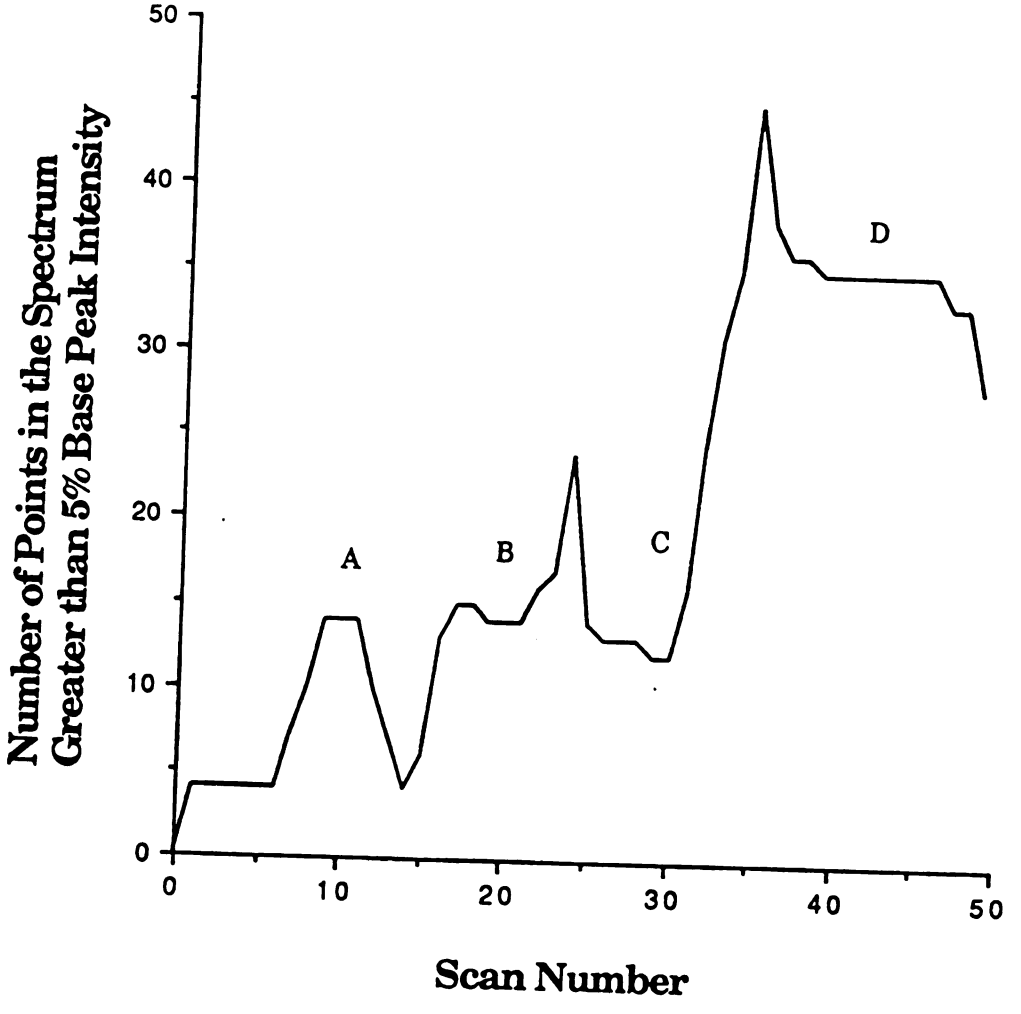
Simply counting the number of peaks in the spectrum will provide information as to the degree-of-fragmentation, but will not eliminate the difficulties caused by noise that were observed using the generic sigma algorithm. Instead, to minimize this problem, a peak threshold was used which required peak intensities to exceed 5% of the base peak. In this manner, contributions to the spectrum from minor components and noise were reduced while only minor peaks in the spectrum were ignored.

A reconstructed chromatogram based on the number of peaks in the spectrum of each scan is included as Figure 4.7. Little difference can be observed in this figure among the responses of the first three compounds. Only octylmercaptan stands out from the rest as having many more peaks in its spectrum. By providing a small window of acceptable number of peaks in the spectrum, the octylmercaptan could be discriminated against, thereby reducing the number of components that require interpretation.

The wing on the left shoulder of the octylmercaptan peak in Figure 4.7 is due to the increased number of mass spectral peaks observed when significant quantities of anthracene are present. Likewise, wings and broadening in the other peaks can be associated with the overlap of eluting component and traces of air, contributing to a larger number of peaks in the spectrum. This problem is most severe when low concentrations of eluting species are present and hence their contribution is limited to the shoulders of the peaks. Figure 4.8 illustrates that the selection of the threshold for peak definition is critical. In this figure, a threshold of 25% of the base peak intensity was used. The aromatic species can now be easily distinguished



4.7. Number of peaks reconstructed chromatogram with a 5% of base peak intensity threshold. Labels marking the centroids for chromatographic peaks are for (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.

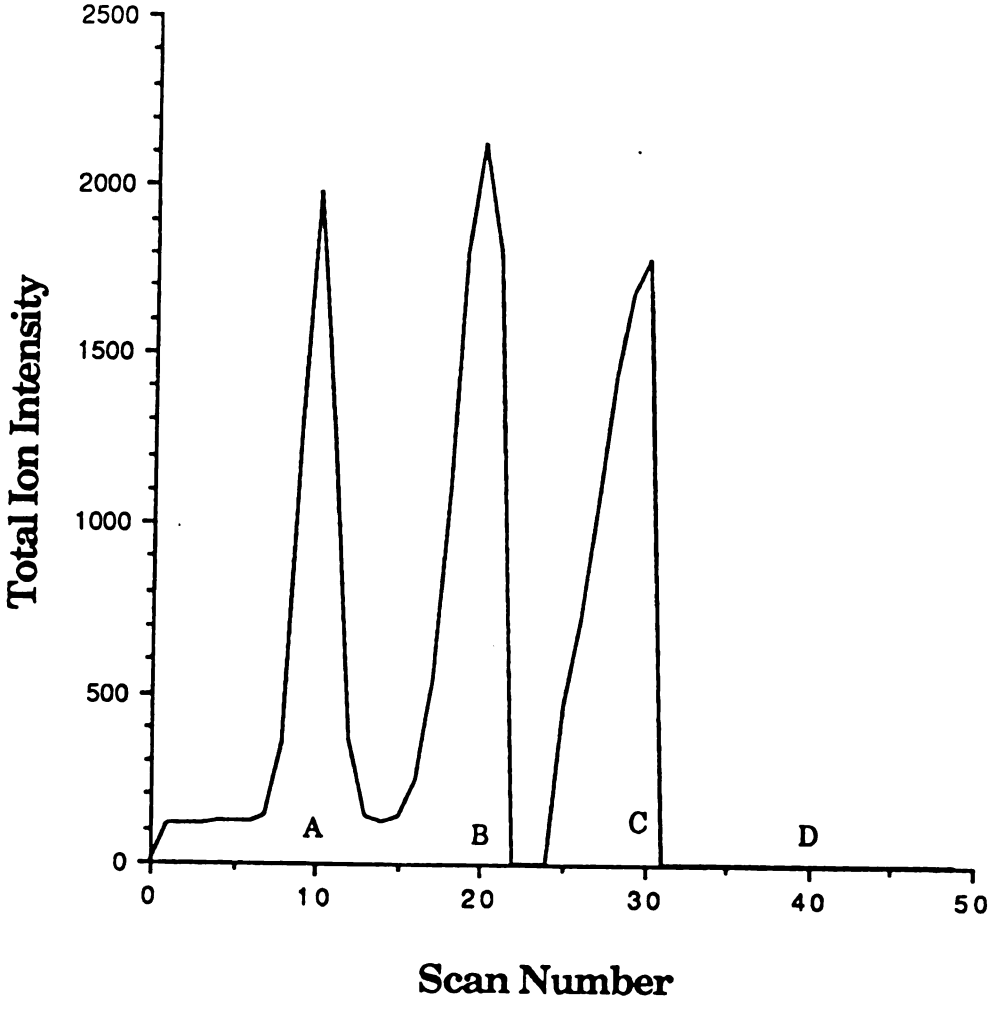


4.8. Number of peaks reconstructed chromatogram with a 5% of base peak intensity threshold. Labels marking the centroids for chromatographic peaks are for (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.

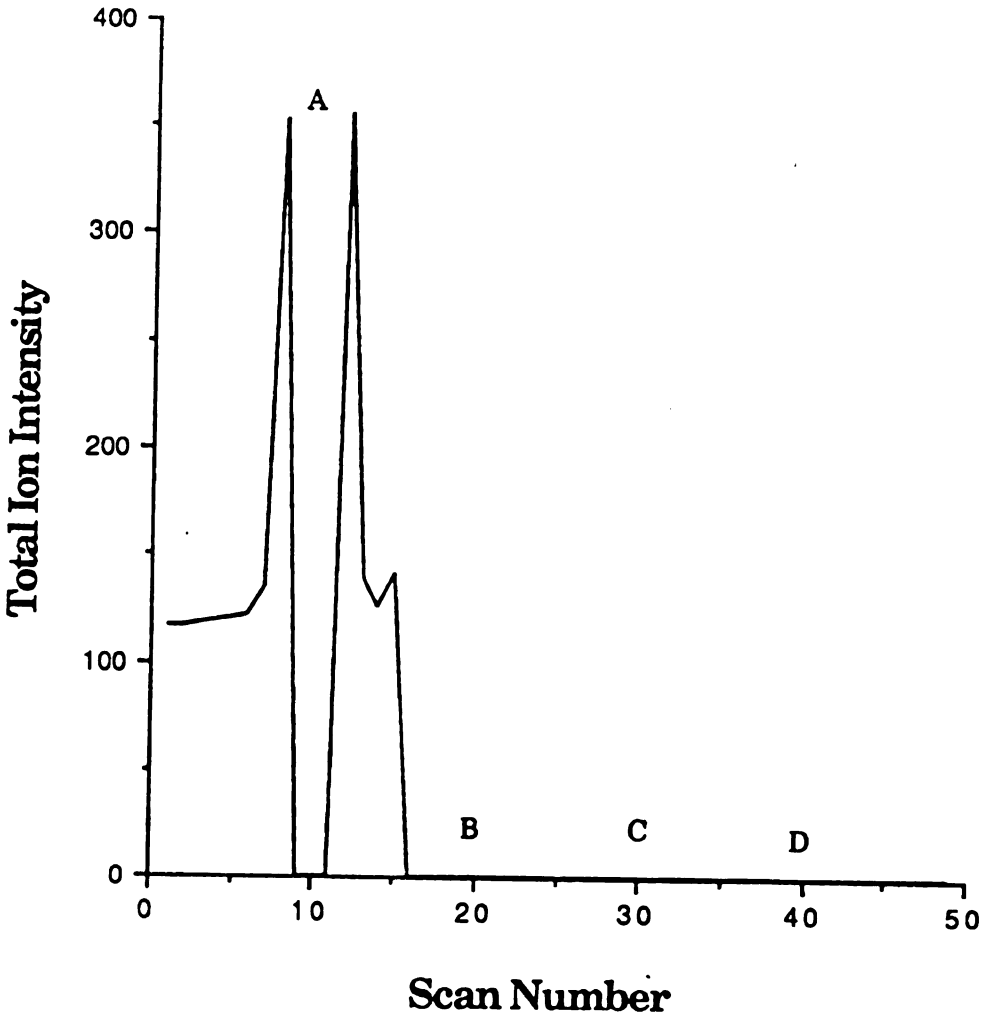
from the aliphatic constituents, but it is difficult to discern the presence of anthracene from the background.

As was done with the generic sigma algorithm, it is possible to pass the total ion intensity to the plot file for those scans in which the number of peaks fall within a predetermined window. This was done to generate data for Figure 4.9. A lower threshold of 3 peaks was used to eliminate the contribution from the air background. An upper threshold limit of 15 peaks was used to permit aromatic species to pass through the filter while discriminating against non-aromatic components. All scans that did not fall into this range resulted in a 0 value being sent to the plot file. Since the overlap region of anthracene and octylmercaptan result in spectra that exceed the permissible number of peaks, the anthracene peak is skewed. This algorithm discriminates against compounds with many peaks in the mass spectrum, such as octylmercaptan. In this way, a concentration-dependent means can be achieved to filter out some of the undesired information. However, Figure 4.9 shows that acrylic acid, which has a similar total number of peaks in its spectrum to that of the aromatic components, is passed through the filter along with the aromatic components.

Care must be taken in the selection of threshold values when using these algorithms based entirely on the number of peaks in the spectrum. This is illustrated by Figure 4.10. With a minimum threshold of 2 peaks, the air background is not discriminated against. A maximum threshold of 8 peaks was insufficient, resulting in a discrimination against all eluting components. Only the shoulders of eluting components pass through the filter.



4.9. Total ion intensity reconstructed chromatogram of the test data set in which only compounds in which the number of peaks (5% threshold) is between 3 and 15 percent are plotted. Labels marking the centroids for chromatographic peaks are for (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.

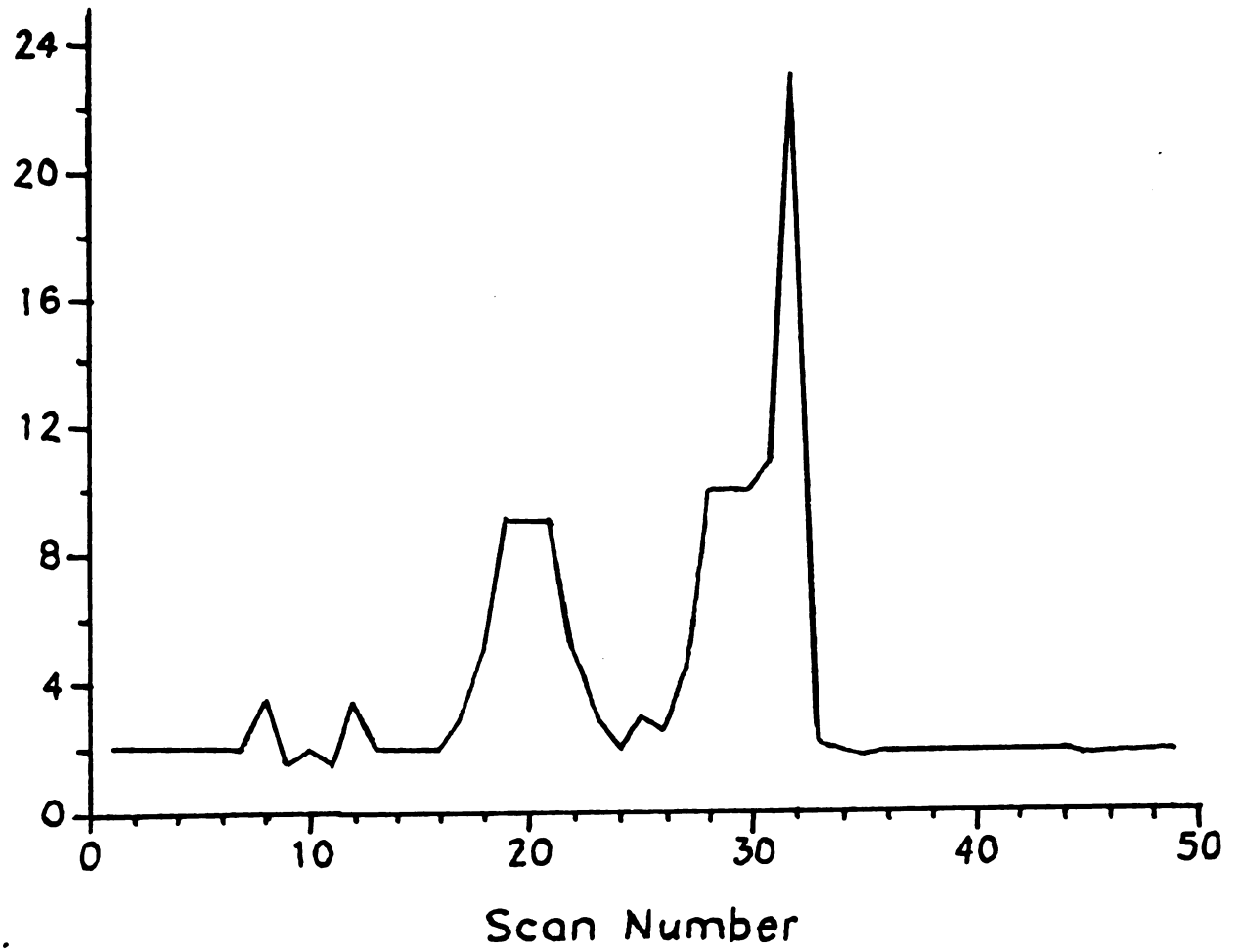


4.10. Total ion intensity reconstructed chromatogram of the test data set in which only compounds in which the number of peaks (5% threshold) is between 2 and 10 percent are plotted. Labels marking the centroids for chromatographic peaks are for (A) acrylic acid, (B) benzene, (C) anthracene, and (D) octylmercaptan.

Combined Algorithm

Algorithms that have been examined to this point have shown some promise in discriminating against species which undergo much fragmentation under electron ionization conditions, but problems still exist. The generic sigma algorithm suffers from too much dependence on the ion intensities to be useful for conventional TOFMS. While the "number of peaks" algorithms are promising, they do not differentiate between spectra with one major peak and many smaller peaks, as in aromatic compounds, and spectra that contain many large peaks, as the acrylic acid. The best features of both algorithms have been combined to develop an algorithm which will meet the objective. This combined algorithm calculates the ratio of the number of peaks whose intensity is greater than 5% of the base peak to the number of peaks whose intensity is greater that 25% of the base peak intensity. Compounds that undergo much fragmentation will have ratios around 1. Species that do not have many fragment ions in their spectra will have high ratios.

The ratio calculated as part of this combined algorithm has been included in Appendix IV under the heading R for ratio. Figure 4.11 is a plot of a reconstructed chromatogram of the test data set using this combined algorithm. Only the aromatic components show significant response in this chromatogram. Wings are still present on the shoulders of the peaks. As the concentration of contaminant species start to increase, the number of peaks in the spectrum will go through a corresponding increase, but the number of peaks above 25% of the base peak will not change significantly until the contaminant becomes a major component. This will cause an increase in the calculated ratio. For those compounds with many peaks in the spectrum, this



4.11. Reconstructed chromatogram of the test data set using the combined algorithm.

increase will be insignificant. However, for compounds with only a few peaks in the mass spectrum this phenomenon is easily observed. The increase becomes noticeable when a species with only a few peaks is contaminated by one with many peaks as is demonstrated by the anthracene peak in Figure 4.11. The use of background subtraction algorithms should minimize the occurrence of this phenomenon from background contaminants. Overlapping chromatographic peaks require more drastic measures ranging from peak deconvolution to reanalysis under different chromatographic conditions.

Conclusions

Without a pure spectrum, results from a degree-of-fragmentation algorithm will be questionable. Difficulties have been observed when using all the degree-of-fragmentation algorithms when a contaminant is present in the form of a high background or an overlapping peak. These problems present themselves as a broadening of the apparent chromatographic resolution or as spikes on the shoulders of chromatographic peaks. Background subtraction algorithms are available on most mass spectrometer data systems and should be used to minimize the contributions from this error source. Alternatively, one could sacrifice the capacity for having a concentration independent method of locating peaks and pass the total ion intensity or the DIFF intensity to the plot file. Overlapping chromatographic peaks present a more serious problem. Two solutions to this problem are available. The first is to collect the data again under different chromatographic conditions which will eliminate the co-elution of components. The second solution involves the use of cleanup algorithms such as that of Biller and Biemann [15].

An interesting phenomenon can be observed in the reconstructed chromatographic profiles of Figures 4.5 and 4.7. When producing plots of scan number against any of the degree-of-fragmentation measurements, a flat-topped peak is observed for each eluent. This is due to the fact that near the chromatographic peak maximum the mass spectrum is less susceptible to significant changes in peak number or intensity from trace contaminants or noisy signals than it is on the shoulders. Those scans that result in the flat-topped chromatographic peaks are also the ideal scans to use for spectral matching. The length of the flat portion of the peak is a function of the number of scans collected across the peak, with high mass spectral generation frequencies producing many clean spectra across the elution profile.

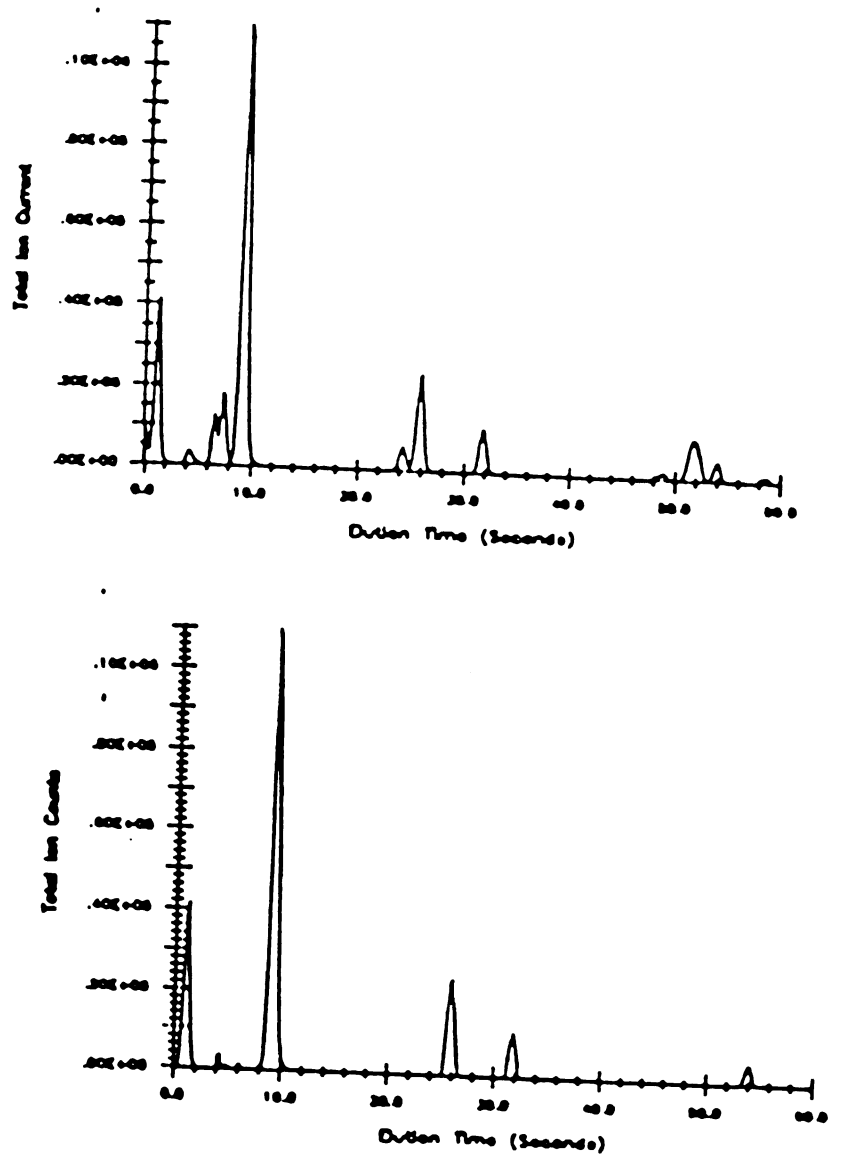
The algorithms that have been developed as part of this work are all based on the degree-of-fragmentation, a close examination of Appendix IV shows that they are not very well correlated with each other. In the extremes, compounds with high values of Σ_g are found to have low values of R as would be expected. However, much fluctuation can be found in the middle of the range. This is due in part to the fact that the value of generic sigma has a much larger dynamic range than does the number of peaks in the spectrum. In addition, the value of generic sigma will distinguish between compounds that undergo one major fragmentation pathway with a few minor pathways and compounds that readily fragment by a few major pathways. This distinction cannot be discerned using any algorithm based exclusively on the number of peaks in the spectrum.

Algorithms discussed in this chapter should be used with caution. They are based on the degree-of-fragmentation and not on the aromaticity of

the molecule. Species that give a high response to these algorithms are not necessarily aromatic. The air contaminant introduced into the test sample is a prime example of a non-aromatic species with a strong response to this algorithm. Other examples are tabulated in Appendix IV. This tabulation gives a good estimate of the predicted degree-of-fragmentation response factors, but these values should be determined for each species under the conditions of analysis.

The algorithms that have been discussed in this chapter have been written to discriminate against those species that produce mass spectra with large amounts of fragmentation. They also can be put to the opposite use. For example, by inverting the combined algorithm ratio strong responses will be found for those eluents that have large amounts of fragmentation and weak responses will be found for those species with little fragmentation. This could ba useful if the sample matrix is heavily contaminated with phthalate esters (plasticizers that produce spectra composed of little more than peaks at m/z 149 and 163) while the desired information regards aliphatic components of the sample matrix.

The real test of any algorithm is to observe its performance under nonideal conditions. Figure 4.12a is the TII reconstructed chromatogram of unleaded gasoline collected at 10 spectra per second. Data from this chromatographic separation were passed through the generic sigma filter, with TII being passed to the plot file to obtain the reconstructed chromatogram in Figure 4.12b. Gasoline is a mixture of alkanes, alkenes,



4.12. Reconstructed chromatograms of unleaded gasoline collected by injecting 0.5 µl gasoline onto a 22 m section of 0.25 mm fused silica tubing coated with 0.25 µm SE-54 and using a mass spectral generation rate of 10 spectra per second. Figures represent (a) the total ion intensity reconstructed chromatogram and (b) the total ion intensity reconstructed chromatogram from only those spectra with generic sigma values between 30 and 60 percent of the base peak intensity.

and light aromatics. As expected, species passed through this algorithm include the benzene, toluene, xylenes, and trimethyl benzenes as was determined through interpretation of the mass spectra. Aliphatic components in the TII chromatogram were discriminated against in the generic sigma plot.

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Appendix I:

Programs Used to Simulate the CVC 2000 Instrument

APPENDIX I
Program CALTOF.FOR

The program in this appendix is used to calculate the intensities and unit-mass-resolution in the CVC 2000 TOFMS. Subprograms and functions include:

CALTOF.FOR -- This subroutine calculates the flight-time of ions of given initial spatial position, initial velocity, and mass.

CUBSOL.FOR -- This subroutine is used to find the solutions to a cubic equation. It is used in the calculation of flight-times.

LIMRES.FOR -- The main program used to set up parameters and cycle through loops of the variable parameters. This is also the portion of the program that writes data files and hence, is used to calculate the percent valley and other pertinent resolution information.

LINE.FOR -- Subroutine to calculate the slope and intercept of a line. This routine is used in the calculation of initial velocities.

MAXMIN.FOR -- Subroutine to find the maximum and minimum intensities of a peak shape. The TOF peak shape does not have a Gaussian distribution and it is not safe to assume that mean positions and velocities in the source will result in the mean flight-time to the detector.

This routine was included to ensure accuracy in the assignment of the proper flight-times.

PRBLTY.FOR -- This function call gives the probability of a value given the mean and variance of the distribution. A normal (Gaussian) distribution is assumed. This function is used to calculate ion intensities.

QDSOL.FOR -- This subroutine is used to find the solution to the quadratic equation. This is needed in the calculation of flight-times.

SIMPS.FOR -- This function performs a Simpson's rule approximation to integrate the area under a curve. It is used in the normalization of intensities.

TPROB.FOR -- This function corrects for ion movement from time lag and then calls the proper subroutines for calculating the probability of ion arrival times. This is the routine that sums the products of position and velocity probabilities.

VELCAL.FOR -- Given values of initial position, mass, and flight-time, this function will calculate the initial velocity that was required. This is based on a series of linear approximations.

```
**************************
*        LIMRES.FOR      *
**************************

*       Eric D. Erickson
*       8/21/87
*
*       Edited 7/6/88 to incorporate delay in reaching max
*              extraction voltage using a model containing 2
*              ideal square wave extraction pulses.
*       Edited 7/14/88 to loop through velocities rather than
*              spatial positions
*       Edited 7/21/88 to calculate velocities assuming a
*              linear relationship between the initial velocity
*              and the final flight-time. This assumption
*              appears to be valid when the initial velocity is
*              small, as is the case when the velocity is caused
*              by kT energy.
*       Edited and included commentary 12/23/88
*       Edited 12/27/88 to incorporate shift in initial
*              position caused by time-lag and new value for
*              ssigma after time-lag.
*       Edited 12/29/88 to correct for calculation of initial
*              position after time-lag. REMEMBER: S0 AND SI ARE
*              DISTANCES TRAVELED IN THE FIRST REGION!!! The
*              spatial time-lag corrections must therefore be
*              subtracted rather than added to the calculations.
*       Edited 1/16/89 to correct for the fact that the flight-
*              time distribution at the detector is not
*              necessarily Gaussian. This means that the mean
*              velocity and position in the ionization region do
*              not necessarily produce the maximum signal
*              intensity at the detector. It was necessary to
*              use a root finding algorithm to locate the flight-
*              time that yields the maximum intensity.
*       Edited 1/18/89 to permit different filenames.
*       Edited 2/28/89 to include accurate determination of
*              valley tof.
*       Edited 3/21/89 to find max and min of tof peak shape
*              through iteration.
*
*       This is the main routine used in the calculation of
*       flight-times and unit mass resolution in the CVC 2000
*       TOFMS. This version of the program calculates the mass
*       of unit mass resolution in time-of-flight mass
*       spectrometry from fundamental principles. Unit mass
*       resolution is defined as that point where the
*       contribution of the M ion to the point midway between M
*       and M+1 is less than a threshold intensity relative to
*       the most probable flight-time for ion M. This is done
*       assuming a normal (Gaussian) distribution of initial
*       velocity and position in the source. Taking a point on
*       the spatial distribution, and its probability of
*       occurrence, the velocity needed to give the desired
```

```
*       flight-times (maximum and valley points) and its
*       probability are calculate. The product of these two
*       probabilities is summed over many spatial positions to
*       obtain probabilities, representative of intensities at
*       these two flight-times for adjacent peaks of equal
*       intensity.
*
*       This program needs to be linked to AUX.FOR, which
*       contains all the necessary subprograms.
*

        PROGRAM LIMRES

************************************************************
*       Variable assignments                               *
************************************************************

        PARAMETER (COUELE = 1.6021892D-19)

        COMMON/ VTIME/ TR          ! Time to maximum extn. voltage
        COMMON/POTDIF/VDIF1,VSUM1,VDIF2,VDIF2B,VDIF3,VDIF4
                                   ! Grid voltages
        COMMON/ POT/ VI, V1, V2, V3
        COMMON/ POS/ D1,D2,D3,D4,D5      ! Grid distances
        COMMON/ PAR1/ SSIGMA, TLAG, S0
        COMMON/ PAR2/ ITER
        COMMON/ PAR3/ MASS, TEMP

        REAL*8 D1                  ! Distances of various regions
        REAL*8 D2                  ! in m
        REAL*8 D3
        REAL*8 D4
        REAL*8 D5
        REAL*8 EM                  ! End mass
        REAL*8 ETL                 ! End time-lag
        REAL*8 EV1                 ! End ion focus
        REAL*8 IFSTEP              ! Ion focus step
        REAL*8 M                   ! Mass in kg
        REAL*8 Mhi
        real*8 mlo
        REAL*8 MASS                ! Mass of the ion
        REAL*8 MSTEP               ! Mass step
        REAL*8 MTLAG               ! Time-Lag in microseconds
        REAL*8 S0                  ! Center position for space
                                   ! distribution
        REAL*8 SI                  ! New center position due to tlag
        REAL*8 SINIT(2)            ! Initial position of the ion
        REAL*8 SM                  ! Start mass
        REAL*8 SSIGMA              ! Std dev of initial position
        REAL*8 STL                 ! Start time-lag
        REAL*8 SV1                 ! start ion focus
        REAL*8 TMAX
        real*8 thi
        REAL*8 TMIN
```

```
      REAL*8 TEMP              ! Source temperature in Kelvin
      REAL*8 TLAG              ! Time-lag
      REAL*8 TLSTEP            ! Time-lag step size
      REAL*8 TOF               ! Flight-time of the ion
      REAL*8 TOFHI             ! Flight-time for M+1 ion
      real*8 toflo
      REAL*8 TR                ! Time to maximum extn. voltage
      REAL*8 V1                ! Ion focus voltage
                               ! Range: 6 to 140
      REAL*8 VI                ! Voltage on grid 1 B4 extraction
      REAL*8 V2                ! Voltage on grid 2
                               ! Range: 150 to 260
      REAL*8 V3                ! Voltage on grid 3
      REAL*8 V4                ! Voltage on grid 4
      REAL*8 VSUM1
      REAL*8 VDIF1
      REAL*8 VDIF2
      REAL*8 VDIF2B
      REAL*8 VDIF3
      REAL*8 VDIF4
      REAL*8 VINIT       ! Initial velocity, corr for tlag
      REAL*8 VSIGMA            ! Std dev of velocity
      REAL*8 TPROB             ! Flight-time Probability
      REAL*8 PROMAX            ! Probability of t(m)
      REAL*8 PROMIN            ! Probability of t(m+.5)

      REAL*4 RATIO             ! PROMIN/PROMAX
      REAL*4 RATLIM            ! Maximum acceptable valley
      REAL*4 PREV              ! Previous ratio

      INTEGER IIF              ! Ion focus increment
      INTEGER IM               ! Mass increment
      INTEGER ITER             ! Number of spatial iterations
      INTEGER ITL              ! Time-lag increment
      INTEGER ICNT             ! Integer counter

      CHARACTER*20 DEST        ! Destination filename

**********************************
*       Initialize Variables     *
**********************************

      D1 = 0.365449D-2         ! Distances in meters
      D2 = 0.17018D-2
      D3 = 0.60706D-2
      D4 = 0.56134D-2
      D5 = 2.10
      S0 = 0.2E-2              ! In meters
      TEMP = 500.              ! In Kelvin
      SSIGMA = 0.01D-2         ! Meters
      Vi = -0.44               ! Negative due to repulsion
      V2 = 215.                ! Grid 2-4 final voltages
      V3 = 1417.
      V4 = 2556.
```

```
      VDIF3 = V3 - V2
      VDIF4 = V4 - V3

*************************************************************
*     Introduction to the program                           *
*************************************************************

      TYPE *, 'Welcome to LIMRES.FOR.  This program '
      TYPE *, 'calculates the unit mass resolution for ions '
      TYPE *, 'in the CVC 2000 instrument, based on the '
      TYPE *, 'initial spatial and velocity distributions of'
      TYPE *, 'ions in the source.'
      TYPE *, ' '

*************************************************************
*     Query for variable quantities                         *
*************************************************************

      TYPE *,'What is the destination filename?'
      READ (5,5) DEST
5     FORMAT(A20)

      TYPE *,' '
      TYPE *,'Enter ranges for variables to be used in '
      TYPE *, 'loops.'
      TYPE *,' '

      TYPE *,'What is the maximum acceptable valley '
      TYPE *,'height?(%)'
      ACCEPT *, RATLIM   ! The contribution of both peaks
                                    ! are calculated in this version.

*     Ion focus is the voltage applied to the first
*     (extraction) grid in the CVC2000 instrument.  This
*     value ranges from 6 to 140 Volts.

10    TYPE *, 'What is the start ion focus? (Volts)'
      ACCEPT *, SV1
      TYPE *, 'What is the end ion focus? (volts)'
      ACCEPT *, EV1
      IF (SV1 .EQ. 0.0) THEN
       V1 = 79.
       VSUM1 = V1 + Vi
       VDIF1 = V1 - Vi
       VDIF2 = V2 - V1
       VDIF2B = V2 - VDIF1
       GO TO 30
      ELSE IF (SV1 .LT. 6.0 .OR. SV1 .GT. 140.) THEN
20     TYPE *,'Outside of range. Legitimate values range '
       TYPE *,'from 6 to 140 Volts.  Try again.'
       GO TO 10
      ELSE IF (EV1 .LT. 6.0 .OR. EV1 .GT. 140.) THEN
       GO TO 20
      ELSE IF (SV1 .EQ. EV1) THEN
```

```
        IFSTEP = 1.
        V1 = SV1
        VSUM1 = V1 + Vi
        VDIF1 = V1 - Vi
        VDIF2 = V2 - V1
        VDIF2B = V2 - VDIF1
        GO TO 30
      ENDIF
      TYPE *,'What is the ion focus step? (Volts/Step)'
      ACCEPT *, IFSTEP
      IIF = INT((EV1 - SV1) / IFSTEP)

*     TOFMS instruments essentially have no maximum mass
*     range. They permit the detection of any ion with
*     enough energy to knock an electron off of the detector.
*     Unless the ion's flight time is within a time window
*     defined by the extraction frequency however, it may be
*     difficult to actually assign a mass to a detector
*     event. For the purposes of this program, negative
*     masses are discarded and positive ones are unlimited.
*     The pulse frequency of the instrument is 10 KHz, but
*     this limitation is not considered in these calculations.

30    TYPE *,''
      TYPE *, 'What is the start mass? (Daltons)'
      ACCEPT *, SM
      TYPE *, 'What is the end mass? (Daltons)'
      ACCEPT *,EM
      IF (SM .LT. 1.0 .OR. EM .LT. 1.0) THEN
        TYPE *,'Mass out of range. Negative values are not'
        TYPE *,'permitted. Try again.'
        GO TO 30
      ELSE IF (SM .EQ. EM) THEN
        GO TO 40
      ENDIF
      TYPE *,'What is the mass step? (Daltons)'
      ACCEPT *,MSTEP
      IM = INT((EM - SM) / MSTEP)

*     Time-lag is a delay time between ion formation and ion
*     extraction out of the source that is used for energy
*     focusing on conventional TOFMS instruments. The CVC-2000
*     has an adjustable time-lag of between 0.0 and 5.0
*     microseconds.

40    TYPE *,''
      TYPE *,'What is the initial time-lag? (microseconds)'
      ACCEPT *,MTLAG
      STL = MTLAG / 1.E6
      TYPE *, 'What is the final time-lag? (microseconds)'
      ACCEPT *, MTLAG
      ETL = MTLAG / 1.E6              ! Convert to seconds
      IF ((STL .LT. 0.0) .OR. (ETL .LT. 0.0)) THEN
45      TYPE *,'Time-lag out of range. The permissible range'
```

```
        TYPE *,'is between 0.0 and 5.0 microseconds. '
        TYPE *,'Try again.'
        GO TO 40
       ELSE IF ((STL .GT. 5.0) .OR. (ETL .GT. 5.0)) THEN
        GO TO 45
       ELSE IF (STL .EQ. ETL) THEN
        GO TO 50
       ENDIF
       TYPE *, 'What is the time-lag step? (microseconds)'
       ACCEPT *, MTLAG
       TLSTEP = MTLAG / 1.E6                ! Convert to seconds
       ITL = INT((ETL - STL) / TLSTEP)

*      This program uses an iteration of spatial position
*      around a mean position, and a calculation of the
*      velocity needed to have an ion start at that position.

50     TYPE *,''
       TYPE *,'How many position iterations are desired? (>=2)'
       ACCEPT *, ITER

*      The flight-time calculations take into consideration
*      that an ideal square wave extraction voltage is
*      impossible to obtain. The operator is therefore able
*      to set a time for a linear ramp to the maximum
*      extraction voltage.

       TYPE *,''
53     TYPE *,'How much time to maximum extraction voltage?
       1       (nsec)'
       ACCEPT *, TR
       IF (TR .LT. 0.0) THEN
        TYPE *,'Negative values do not make sense. Try again.'
        GO TO 53
       ENDIF
       TR = TR * 1.E-9                      ! Convert to seconds

55     TYPE *,''
       TYPE *,'The calculations have begun'

       OPEN (UNIT=1, FILE=DEST, STATUS='NEW')
       OPEN (UNIT=2, FILE='LIM.DAT', STATUS='NEW')

*************************************************************
*      Initiate calculations                                *
*************************************************************

       IF ((SV1 .EQ. EV1) .OR. (SV1 .EQ. 0.0)) GO TO 60
       DO 2000 I = 0, IIF                   ! Start ion focus loop
        V1 = SV1 + FLOAT(I) * IFSTEP        ! Set ion focus
        VSUM1 = V1 + Vi
        VDIF1 = V1 - Vi
        VDIF2 = V2 - V1
        VDIF2B = V2 - VDIF1
```

```
60        IF (SM .EQ. EM) THEN              ! Check for single mass
           MASS = SM
           GO TO 70
          ENDIF

          DO 500 J = 0, IM                  ! Start mass loop
           MASS = SM + FLOAT(J) * MSTEP! Set mass

70         Mhi = (MASS + 1.D0) * 1.6605655d-27
           Mlo = (MASS - 1.D0) * 1.6605655d-27
        PREV = 100.
        ICNT = 0
         IF (STL .EQ. ETL) THEN         ! Check for single time-lag
          TLAG = STL
          GO TO 80
         ENDIF

*       Assumption: Ions stay put until the electron beam is
*       turned off.

         DO 1000 K = 0, ITL             ! Start time-lag loop
          TLAG = STL + FLOAT(K) * TLSTEP          ! Set time-lag
80        SI = S0-((COUELE*Vi*TLAG*TLAG)/(2.*Mhi*D1))
          VINIT = COUELE*TLAG*Vi/(Mhi*D1)
          CALL CALTOF (SI, VINIT, Mhi, TOFHI)    ! TOF for M+1
          SI = S0-((COUELE*Vi*TLAG*TLAG)/(2.*Mlo*D1))
          VINIT = COUELE*TLAG*Vi/(Mlo*D1)
          CALL CALTOF (SI, VINIT, Mlo, TOFlo)     ! TOF for M-1

          CALL MAXMIN (TOFLO, TOFHI, PROMAX, PROMIN)
          IF (PROMAX .EQ. 0.0D0) GO TO 1000
                                          ! Avoid division by 0
          RATIO = 100. * PROMIN / PROMAX          ! Percent
          WRITE (2,121) MASS,TLAG*1.E6, PROMIN, PROMAX, RATIO
          IF ((RATIO .GT. PREV) .AND. (TLAG .GT. 2.E-6) .AND.
     1        (RATIO .GE. RATLIM)) THEN
           WRITE (1,110) MASS, TLAG*1.E6
110        FORMAT (2X, F5.0, '        ', F7.2)
           ICNT = 0
           GO TO 490
          ELSE IF (ICNT .EQ. 0) THEN
           IF ((RATIO.LE.PREV) .AND. (RATIO.LE.RATLIM)) THEN
               WRITE (1,110) MASS, TLAG*1.E6
                     ICNT = 1
           ENDIF
          ENDIF
120       FORMAT (2X, F5.0, 4('        ', F7.2))
121       FORMAT (2X, F5.0, '        ', F7.2, 3('        ', e12.4))
          PREV = RATIO
510       IF (STL .EQ. ETL) GO TO 490
1000     CONTINUE                           ! end time-lag loop
490      TYPE *, 'MASS',MASS,'DONE'
         PREV = 100.
           IF (SM .EQ. EM) GO TO 1010
```

```
500       CONTINUE                          ! End mass loop
1010    IF (SV1 .EQ. EV1) GO TO 2010
2000    CONTINUE                          ! End ion focus loop
2010    CLOSE (1)
        CLOSE (2)

        TYPE *, 'Your data have been stored in ', DEST
        END


*****************************************************
*       CALTOF.FOR
*****************************************************
*
*       Eric D. Erickson
*       6/29/88
*       Edited 7/2/88
*       Edited to model 2 square waves 7/6/88
*       Math correction 7/7/88
*       Math correction 7/28/88
*       Math correction 8/8/88
*       Math correction 12/22/88
*
*       This program was written due to my frustration with
*       earlier versions of the CVC simulation. This version
*       calculates the flight-times of an ion of mass M (in kg)
*       given its initial position (in m) and velocity (in m/s)
*       in the CVC 2000 source. Other versions of this program
*       have been written and adapted from George Yefchak's
*       simulations, but this one is a significant variation
*       from those programs which are based on initial ion
*       energy rather than velocity as in this program. In
*       part, this program was written to see if I could get it
*       to work (i.e. if I understand all the concepts
*       correctly) and in part it was written to simplify the
*       incorporation of the time that it takes for the
*       extraction pulse to reach its maximum voltage.
*
*       This derivation is based on the following fundamental
*       relationships:
*
*               a = dv/dt
*               a = qV/md
*               v = dx/dt
*
*       Derivations of the individual expressions used in this
*       program are in my notebook dated 7/28/88. The
*       correction of time needed to reach maximum voltage is
*       done using a model consisting a linear ramp between the
*       initial and final voltages. This version now includes
*       the remote possibility that ions may enter the third
*       region of the source before the maximum voltage is
*       obtained. The model used for this program will permit
```

```
*       the entry of 0 ns if a single ideal square wave
*       extraction pulse is desired.
*
        SUBROUTINE CALTOF(SINIT, VINIT, M, TOF)

        PARAMETER (COUELE = 1.6021892D-19)

        COMMON/ VTIME/ TR
        COMMON/ POTDIF/ VDIF1,VSUM1,VDIF2,VDIF2B,VDIF3,VDIF4
        COMMON/ POT/ Vi, V1, V2, V3
        COMMON/ POS/ D1,D2,D3,D4,D5

        REAL*8 V1               ! Final voltage on grid 1
        REAL*8 Vi               ! Initial voltage on grid 1
        REAL*8 V2
        REAL*8 V3
        REAL*8 VSUM1            ! V1 + Vi
        REAL*8 VDIF1            ! V1 - Vi
        REAL*8 VDIF2            ! V2 - V1
        REAL*8 VDIF2B           ! V2 - VDIF1
        REAL*8 VDIF3            ! V3 - V2F
        REAL*8 VDIF4            ! V4 - V3
        REAL*8 A                ! Variables for quadratic solution
        REAL*8 B
        REAL*8 C
        REAL*8 CS2              ! Cubic solutions
        REAL*8 CS3
        REAL*8 M                ! Ion mass in kg
        REAL*8 SINIT            ! Initial ion position in m
        REAL*8 VINIT            ! Initial ion velocity in m/s
        REAL*8 TMP1             ! couele*q/m*d
        REAL*8 TMP2
        REAL*8 TMP3
        REAL*8 TMP4
        REAL*8 D1               ! Grid distances
        REAL*8 D2
        REAL*8 D3
        REAL*8 D4
        REAL*8 D5
        REAL*8 RTIME
        REAL*8 T1               ! Time spent in various regions
        REAL*8 T2
        REAL*8 T3
        REAL*8 T4
        REAL*8 T5
        REAL*8 TOF              ! Time-of-Flight for the ion
        REAL*8 TR       ! Time for voltage ramp to grids 1 and 2
        REAL*8 XTMP     ! Second solution to quadratic eqn.
        REAL*8 VEL1             ! Velocities leaving regions
        REAL*8 VEL2
        REAL*8 VEL3
        REAL*8 VEL4

        INTEGER I,J             ! Counters
```

```
*       INITIALIZE VARIABLES
*       ASSUMPTION: All ions are singly charged.
*       If not, then the TMP variables need to be multiplied by
*       the number of charges on the ion.

        TMP1 = COUELE / (M * D1)
        TMP2 = COUELE / (M * D2)
        TMP3 = COUELE / (M * D3)
        TMP4 = COUELE / (M * D4)

*       IN REGION 1

        IF (TR .EQ. 0.0) then           ! Avoid division by 0
                T1 = 1.
                GO TO 10
        ENDIF

*       tr greater than t1

        A = 3. * TR * V1 / VDIF1
        B = 6. * TR * VINIT / (TMP1 * VDIF1)
        C = -(6. * SINIT * TR / (TMP1 * VDIF1)) - SINIT
        CALL CUBSOL(A, B, C, T1, CS2, CS3)          ! Calculate t1
        IF (T1 .LT. CS2) T1 = CS2       ! Take highest solution
        IF (T1 .LT. CS3) T1 = CS3
        VEL1 = (TMP1*Vi*T1) + (TMP1*VDIF1*T1*T1/2.*TR) + VINIT

*       tr <= t1

10      IF (TR .LE. T1) THEN
                A = TMP1 * V1 / 2.
                B = (TMP1 * VSUM1 * TR / 2.) + VINIT
                C = (TMP1*TR*TR*(V1+2*Vi)/6.) + VINIT*TR - SINIT
                CALL QDSOL(A, B, C, XTMP, T1)
                IF (T1 .LT. XTMP) T1 = XTMP! Take highest soln
                VEL1 = (2. * A * T1) + B
                T1 = T1 + TR
                IF (T1 .LT. TR) THEN ! Remove impossible times
                        T1 = 0.0D0
                        VEL1 = VINIT
                ENDIF
        ENDIF

*       IN REGION 2

*       tr < t1

        IF (TR .LE. T1) THEN
                A = TMP2 * VDIF2 / 2.0
                CALL QDSOL(A, VEL1, -D2, XTMP, T2)
                IF (T2 .LT. XTMP) T2 = XTMP
                VEL2 = 2. * A * T2 + VEL1
```

```
      ELSE

*     tr > t1 + t2

            RTIME = TR - T1
            A = -3.*Vi*TR/VDIF2B
            B = 6.*TR*VEL1/(VDIF2B*TMP2)
            C = -6.*TR*D2/(VDIF2B*TMP2)
            CALL CUBSOL(A, B, C, T2, CS2, CS3)
            IF (T2 .LT. CS2) T2 = CS2       ! Take highest soln
            IF (T2 .LT. CS3) T2 = CS3
            VEL2 = (TMP2*VDIF2B*T2*T2/(2.*TR))-
     1             (Vi*TMP2*T2)+VEL1

*     t1 < tr <= t1 + t2

            IF (TR .LE. T1+T2) THEN
              A = TMP2 * VDIF2 / 2.
              B = (TMP2*RTIME*(VDIF2-Vi)/(2.*TR)) + VEL1
              C = (TMP2*(VDIF2-(2.*Vi))*RTIME*
     1             RTIME*RTIME/(6.*TR))-
     2             (TMP2*Vi*RTIME*RTIME/2.)+(VEL1*RTIME)-D2
              CALL QDSOL(A, B, C, XTMP, T2)
              IF (T2 .LT. XTMP) T2 = XTMP ! Take highest soln
              VEL2 = (TMP2*VDIF2*T2)+(TMP2*(VDIF2Vi)*RTIME/
     1             (2.*TR))+VEL1
              T2 = T2 + TR - T1
            ENDIF
      ENDIF

*     IN REGION 3

*     tr < t1 + t2

      IF (TR .LE. T1 + T2) THEN
            A = TMP3 * VDIF3 / 2.
            CALL QDSOL(A, VEL2, -D3, XTMP, T3)
            IF (T3 .LT. XTMP) T3 = XTMP          ! Take highest soln
            VEL3 = 2. * A * T3 + VEL2
      ELSE
            RTIME = RTIME - T2

*     tr > t1 + t2 + t3

            A = -3.*TR*V3/V2
            B = -6.*TR*VEL2/(TMP3*V2)
            C = -B*D3/VEL2
            CALL CUBSOL(A, B, C, T3, CS2, CS3)
            IF (T3 .LT. CS2) T3 = CS2       ! Take highest soln
            IF (T3 .LT. CS3) T3 = CS3
            VEL3 = (TMP3*V3*T3) - (TMP3*V2*T3*T3/(2.*TR)) + VEL2
```

```
*       t1 + t2 < tr <= t1 + t2 + t3

              IF (TR .LE. T1+T2+T3) THEN
                A = TMP3 * VDIF3 / 2.
                B = (TMP3*V3*RTIME)-
     1                (TMP3*V2*RTIME*RTIME/(2.*TR))+VEL2
                C = (TMP3*V3*RTIME*RTIME/2.)-
     1                (TMP3*V2*RTIME*RTIME*RTIME/
     2                (6.*TR))+(VEL2*RTIME)-D3
                CALL QDSOL(A, B, C, XTMP, T3)
                IF (T3 .LE. XTMP) T3 = XTMP ! Take highest soln
                VEL = (2. * A * T3) + B
                T3 = T3 + TR - T1 - T2
              ENDIF
       ENDIF

*      REGION 4

       A = TMP4 * VDIF4 / 2.0
       CALL QDSOL(A, VEL3, -D4, XTMP, T4)
       IF (T4 .LT. XTMP) T4 = XTMP
       VEL4 = 2. * A * T4 + VEL3

*      REGION 5: DRIFT TUBE

       T5 = D5 / VEL4

*      TOTAL FLIGHT TIME

       TOF = T1 + T2 + T3 + T4 + T5          ! In seconds

*      QUIT SUBROUTINE

1000   RETURN
       END


****************************************
*      CUBSOL.FOR
****************************************
*
*      Eric D. Erickson
*      8/8/88
*
*      This routine takes 3 values, A, B, and C, and
*      calculates the real roots of the cubic equation:
*
*              0 = x**3 + A*X**2 + B*X + C
*
*      The algorithm used is derived from one given on page
*      157 of NUMERICAL RECIPES IN C.  All variables must be
*      REAL*8.
*
```

```
      SUBROUTINE CUBSOL (A,B,C,X1,X2,X3)

      REAL*8 A, B, C
      REAL*8 X1, X2, X3
      REAL*8 Q, R, THETA
      REAL*8 THIRD, TMPQ, TMPR, PI2

      THIRD = 1. / 3.
      PI2 = 6.283185307

      Q = (A - 3. * B) / 9.
      R = (2.*(A**3) - 9.*A*B + 27.*C) / 54.
      TMPQ = Q * Q * Q
      TMPR = R * R

      IF (TMPQ .GT. TMPR) THEN          ! There are 3 real roots
            THETA = DACOS(R / SQRT(TMPQ))
            X1 = -2.*SQRT(Q)*DCOS(THETA/3.) - A/3.
            X2 = -2.*SQRT(Q)*DCOS((THETA+PI2)/3.) - A/3.
            X3 = -2.*SQRT(Q)*DCOS((THETA+2.*PI2)/3.) - A/3.

      ELSE                              ! There is only 1 real root
            TMP = (SQRT(TMPR-TMPQ) + ABS(R))**THIRD
            X1 = -DSIGN(1.D0,R) * (TMP + Q/TMP) - A/3.
      ENDIF

      RETURN
      END


*****************************************
*     LINE.FOR
*****************************************
*
*     Eric D. Erickson
*     12/29/88
*
*     Subroutine to calculate the slope and intercept of a
*     line.
*
      SUBROUTINE LINE (X1,Y1,X2,Y2,M,B)

      REAL*8 X1           ! Coordinates of 2 points on the line
      REAL*8 X2
      REAL*8 Y1
      REAL*8 Y2
      REAL*8 M                  ! Slope
      REAL*8 B                  ! Intercept

      M = (Y1 - Y2) / (X1 - X2)
      B = Y2 - X2 * M

      RETURN
      END
```

```
****************************************
*       MAXMIN.FOR
****************************************
*
*       Eric D. Erickson
*       3/21/89
*
*       Routine to find the maximum and minimum intensities of
*       a peak shape. This routine was written due to problems
*       with the search algorithms previously used. This
*       algorithm searches for the limits using a bin filling
*       approach.
*
*       Edited 4/5/89 to permit the normalization of peak
*       areas.
*
*       Edited 4/7/89 to include a Simpson's approximation of
*       the area
*

      SUBROUTINE MAXMIN(X1, X2, RMAX, RMIN)

      PARAMETER(POINTS = 50.)

      REAL*8 X1, X2                     ! Limiting flight-times
      REAL*8 TMAX                 ! Flight-time for peak maximum
      REAL*8 RMAX, RMIN           ! Probabilities of max and min
      REAL*8 INCR                 ! Flight-time increment
      REAL*8 TIME                 ! Flight-time
      REAL*8 IONPROB(50)                ! TOF probability
      REAL*8 TOTPROB                    ! Total probability
      REAL*8 SIMPS          ! Simpson rule approximation of area

*     Initialize variables

      TOTPROB = 0.0
      INCR = (X2 - X1) / POINTS
      RMAX = -10.0
      RMIN = 1000.0
      TMAX = 1.

*     Find TOF with the max and min probability
      DO 10 I=1,POINTS
            TIME = X1 + FLOAT(I) * INCR
            IONPROB(i) = TPROB(TIME)
            IF (IONPROB(i) .GT. RMAX) THEN
                  RMAX = IONPROB(i)
                  TMAX = TIME
            ENDIF
            IF ((IONPROB(i).LT.RMIN).AND.(TIME.GT.TMAX))
     1            RMIN = IONPROB(i)
```

```
            IF ((IONPROB(I).GT.RMIN).AND.(TIME.GT.TMAX))
     1              GO TO 15
10   CONTINUE

*    Normalize intensities

15   TOTPROB = SIMPS(1, I, IONPROB)
     IF (TOTPROB .EQ. 0.0) THEN
          TYPE *, 'Divide by zero error occurred in area.'
          GO TO 20
     ENDIF
     RMAX = RMAX / TOTPROB
     RMIN = RMIN / TOTPROB

20   RETURN
     END


****************************************
*    PRBLTY.FOR
****************************************
*
*    Eric D. Erickson
*    1/29/88
*    Changed to a function call 7/14/88
*
*    This subroutine calculates the probability of an
*    occurrence, assuming a normal (Gaussian) distribution of
*    events. This uses the relationship:
*
*          P(x) = exp((x-u)**2/2(sigma)**2)
*
     FUNCTION PRBLTY (X, SIGMA, MEAN)

     REAL*8 DEV              ! Deviation
     REAL*8 MEAN                  ! Mean position
     REAL*8 SIGMA                 ! Std dev about mean
     REAL*8 X                ! True position
     REAL*8 PRBLTY                ! Probability

     DEV = X - MEAN
     PRBLTY = EXP(-(DEV * DEV) / (2. * SIGMA * SIGMA))

     RETURN
     END
```

```
**********************************************
*       QDSOL.FOR
**********************************************
*
*       Eric D. Erickson
*       6/30/88
*
*       This subroutine finds the two solutions to the
*       quadratic equation and returns them as X1 and X2.  All
*       variables must be declared as REAL*8.  I have not taken
*       the time to fix this for imaginary numbers, so
*       imaginary numbers are passed as -1.
*
*       Edited to reduce possible errors on 7/8/88.  The method
*       used is that described on page 156 of NUMERICAL
*       RECIPES IN C.
*
*               Edited to eliminate division by zero 1/17/89.
*
        SUBROUTINE QDSOL(A, B, C, X1, X2)

        REAL*8 A                        ! All symbols are commonly used
        REAL*8 B                        ! ones in general Algebra
        REAL*8 C
        REAL*8 Q
        REAL*8 ROOT             ! Temporary value to check for real
                                        ! roots of the equation
        REAL*8 X1                       ! Two solutions
        REAL*8 X2

        ROOT = B * B - 4. * A * C
        IF (ROOT .LT. 0.0) THEN
                X1 = -1.D10
                X2 = -1.D10
                RETURN
        ENDIF
        Q = -0.5 * (B + DSIGN(1.0D0, B) * SQRT(ROOT))
        X1 = Q / A
        IF (Q .EQ. 0.0) THEN
                X2 = -1.D10
                RETURN
        ENDIF
        X2 = C / Q

        RETURN
        END
```

```
*********************************
*       SIMPS.FOR
*********************************
*
*       Simpson's rule approximation
*
*       This function is a modification of SIMPS() from George
*       Yefchak dated April 1985.  It was modified and input by
*       Eric D. Erickson on 4/7/89.
*

        FUNCTION SIMPS (A, B, FUN)

        REAL*8 FUN(50)                  ! Array of peak heights
        REAL*8 SUM                      ! Sum of peak areas
        REAL*8 SIMPS                    ! Simpson's area

        INTEGER A                       ! Counters
        INTEGER B

        SUM = 0.0
        IF (MOD((B - A), 2) .NE. 0) THEN        ! If not even
                SUM = SUM+3.0*FUN(B) ! Add rectangular area from
                B = B - 1               ! last interval and make it even
        ENDIF
        DO 10 I = A+1, B-2, 2
                SUM = SUM + 4.0 * FUN(I) + 2.0 * FUN(I+1)
10      CONTINUE

        SUM = SUM + FUN(A) + 4.0 * FUN(B-1) + FUN(B)
        SUM = SUM / 3.0
        SIMPS = SUM
        RETURN
        END


************************************
*       TPROB.FOR
************************************
*
*       Eric D. Erickson
*       1/16/89
*
*       Function to calculate probability of a particular
*       flight time.
*
*       SINIT is the ion's position when the time-lag ends.
*       VEL is the ion's velocity at the end of the time-lag.
*       XINIT and VINIT are these values immediately upon
*       cessation of ion formation (the electron beam is turned
*       off).
*
```

```
*       Modified 2/28/89 to permit the calculation to include
*       adjacent peak contributions. This was done to enable
*       the search for the true position of the valley.
*
*       Modified 4/5/89 to loop through equidistant spatial
*       positions in the source.
*
      FUNCTION TPROB(TOF)

      PARAMETER (COUELE=1.6021892D-19, BOLTK=1.380662D-23)

      COMMON/ PAR1/ SSIGMA, TLAG, S0
      COMMON/ PAR3/ MASS, TEMP
      COMMON/ POS/ D1,D2,D3,D4,D5      ! Grid distances
      COMMON/ PAR2/ ITER
      COMMON/ POT/ VI, V1, V2, V3

      REAL*8 SIGMAS              ! SSIGMA corrected for time-lag
      REAL*8 Vi                  ! Initial voltage on grid 1
      REAL*8 V1                  ! Final voltage on grid 1
      REAL*8 V2                  ! Final voltage on grid 2
      REAL*8 V3                  ! Grid 3 voltage
      REAL*8 TOF                 ! Flight time
      REAL*8 M                   ! Mass in kg
      REAL*8 S0                  ! Initial mean position
      REAL*8 SI                  ! Mean position
      REAL*8 VSIGMA              ! Velocity sigma
      REAL*8 SINIT               ! Initial Position
      REAL*8 TLAG                ! Time-lag in seconds
      REAL*8 MASS          ! Mass in Daltons
      REAL*8 TEMP          ! Temperature in Kelvin
      REAL*8 D1                  ! Region 1 distance
      REAL*8 D2                  ! Region 2 distance
      REAL*8 D3                  ! Region 3 distance
      REAL*8 D4                  ! Region 4 distance
      REAL*8 D5                  ! Region 5 distance
      REAL*8 PINC                ! Probability increment
      REAL*8 VEL                 ! Velocity
      REAL*8 VELCAL              ! Calculated velocity
      REAL*8 XINIT               ! Corr init position
      REAL*8 SSIGMA              ! Position Std. Dev.
      REAL*8 VINI                ! Corr init velocity
      REAL*8 TPROB               ! Probability of time tof
      REAL*8 SPROB               ! Positional probability
      REAL*8 VPROB               ! Velocity probability

      INTEGER ITER

      TPROB = 0.0
      DO 200 N = 1,2
       M = (MASS + FLOAT(N-1)) * 1.6605655D-27
       SI = S0-((COUELE*vI*TLAG*TLAG)/(2.*M*D1))
       VSIGMA = SQRT(BOLTK * TEMP / M)
       DO 100 L = 1, ITER                ! Start spatial loop
```

```
          SINIT = 0.0005 + FLOAT(L) * (D1 - 0.0005) /
     1         FLOAT(ITER)
          IF ((SINIT .LT. 0.0D0).OR.(SINIT .GT. D1)) GOTO 100
          VEL = VELCAL(SINIT, M, TOF)
          VINI = VEL - COUELE * Vi * TLAG / (M * D1)
          XINIT = SINIT+COUELE*Vi*TLAG*TLAG/(2.*M*D1)
     1         +VINI*TLAG
          IF ((XINIT.LT.0.0D0) .OR. (XINIT.GT.D1)) GO TO 100
                                ! Throw out ions outside of the source
          SPROB = PRBLTY(XINIT, SSIGMA, S0)
          VPROB = PRBLTY(VINI, VSIGMA, 0.0D0)
          TPROB = TPROB + SPROB * VPROB
100       CONTINUE                              ! End probability loop
200       CONTINUE
          RETURN
          END


************************************
*         VELCAL.FOR
************************************
*
*         Eric D. Erickson
*         12/28/88
*
*         This program calculates the velocity needed to achieve
*         a given flight-time from known initial positions and
*         masses.  A linear approximation is used.
*
*         Edited 1/5/89 to speed up calculations of outliers.  If
*         the velocity is greater than 3000 m/s or less than -
*         3000 m/s, the program now comes to a guess that has
*         more error than smaller velocities, but since the
*         probability of these high velocities is so small to
*         begin with, (<2.4e-5 for m/z 10), these velocities
*         would receive a much smaller weighting in the main
*         program anyway.
*
          FUNCTION VELCAL (POS, M, TOF)

          REAL*8 POS            ! Distance traveled in the first
                                                ! region of the source.
          REAL*8 M                      ! Mass of the ion in kg
          REAL*8 TOF                    ! Expected flight-time
          REAL*8 VELCAL                 ! Calculated velocity
          REAL*8 TOF1           ! TOF of ion with velocity -1000
          REAL*8 TOF2           ! TOF of ion with velocity 1000
          REAL*8 INTER                  ! TOF intercept
          REAL*8 SLOPE                  ! Slope of the line
          REAL*8 X1                     ! Temporary positions
          REAL*8 X2

          INTEGER N                     ! Counter
```

```
*       Initialize variables

        SLOPE = 0.0D0
        INTER = 0.0D0
        X1 = 0.0D0
        X2 = 5.0D2

*       Calculate flight time for 2 points on the line and
*       calculate the slope and intercept of that line.

        CALL CALTOF (POS, X1, M, TOF1)
        IF (TOF .LE. TOF1) THEN
100             CALL CALTOF (POS, X2, M, TOF2)
                IF (TOF .GE. TOF2) THEN
                        CALL LINE (X1, TOF1, X2, TOF2, SLOPE, INTER)
                        GO TO 300
                ELSE
                        N = N + 1
                        IF (N .GT. 6) GO TO 210
                        X1 = X2
                        TOF1 = TOF2
                        X2 = X2 + 5.D2
                ENDIF
                GO TO 100
        ELSE
                X2 = -5.E2
200             CALL CALTOF (POS, X2, M, TOF2)
                IF (TOF .LE. TOF2) THEN
210                     CALL LINE (X1, TOF1, X2, TOF2, SLOPE, INTER)
                        GO TO 300
                ELSE
                        N = N + 1
                        IF (N .GT. 6) GO TO 210
                        X1 = X2
                        TOF1 = TOF2
                        X2 = X2 - 5.D2
                ENDIF
                GO TO 200
        ENDIF

*       Calculate the velocity.

300     VELCAL = (TOF - INTER) / SLOPE

        RETURN
        END
```

Appendix II:

Programs Used to Calibrate the CVC 2000 Instrument

APPENDIX II

Program CVCMASS.FOR

Programs used in TAD calibration.

1. CVCMAS - This is the main program in the calculation of m/z values from flight-times and handles operator interaction. Options are offered for computer calculation of linear parameters from a data file, or operator entry of critical parameters.

2. FILEIO - This subroutine prompts for source and destination filenames and passes them back to the calling program.

3. CALIB - This subroutine calculates the linear calibration parameters.

4. FILCAL - This subroutine is used to derive the calibration parameters and perform a statistical analysis of them. It uses approximate flight-times for three different "known" m/z values and searches the data file for all occurrences of these values within a 15 nsec window, ignoring ions with intensities below 50 counts. Values of k and C as well as their sample standard deviations are output to the terminal.

5. FILDAT - This subroutine takes the calibration parameters and uses them to reduce time/intensity pairs in the source file to mass/intensity pairs and write them to the destination file. In addition, if the mass is not within 0.15 Daltons of a unit mass, an error message is also printed to the destination file. This latter event makes it easy to locate the 80 nsec shift.

```
**********************
*       CVCMASS.FTN       *
**********************
*       Version: July 3, 1987
*       Edited 8/24/88 to include changes to ITR output format.
*
*       Eric D. Erickson
*
*       PURPOSE:
*       This program inputs a flight time and calculates the
*       m/z for data collected on the CVC-TOFMS.  This can now
*       be done using a file that has been ported over from the
*       ITR.
*
        PROGRAM CVCMAS

        REAL*4 TIME                 ! Flight time
        REAL*4 K                    ! Slope
        REAL*4 C                    ! Intercept
        REAL*4 MASS                 ! Mass to charge ratio

        CHARACTER*1 A                       ! Space
        CHARACTER*1 B                       ! Response
        CHARACTER*1 A2                      ! Data source response
        CHARACTER*15 SOURCE                 ! Source filename
        CHARACTER*15 DEST                   ! Destination filename

        TYPE *,'Welcome to CVCMASS.FTN'
        DATA A/' '/                 ! Define space
        WRITE (5,1) (A, I=1,3)
1       FORMAT (A)

*       Where are the data coming from?
        TYPE *,'Are the data to be input from a File '
        TYPE *, 'or the Keyboard?'
        READ (5,1) A2
        IF (A2 .EQ. 'f') A2 = 'F'
        IF (A2 .EQ. 'F') CALL FILEIO (SOURCE, DEST)

*       Is calibration routine needed?
        TYPE *, 'Do you want me to calibrate the data?'
        READ (5,1) B
        IF (B .EQ. 'y') B = 'Y'
        IF (B .EQ. 'Y') THEN
                CALL CALIB (SOURCE, DEST, K, C, A2)
                                    ! Calibrate if answer is yes
        ELSE
                TYPE *, 'What is the value of k?'
                ACCEPT *, K
                TYPE *, 'What is the value of C?'
                ACCEPT *, C
                WRITE (5,1) (A, I=1,2)
        END IF
```

```
      IF (A2 .EQ. 'F') THEN
                  ! Do calculations if files are used
            CALL FILDAT (SOURCE, DEST, K, C)
            GO TO 20
      END IF

5     TYPE *, 'What is the ion flight-time in microseconds?'
      READ (5, 10, END=20) TIME  ! End input upon ^Z
10    FORMAT (E15.6)
      MASS = ((TIME - C)/K)**2
      TYPE *, 'The m/z value is: ', MASS
      GO TO 5

20    END

*************************
*     SUBROUTINE FILEIO      *
*************************
*     This subroutine obtains the source and destination
*     filenames for i/o operations.

      SUBROUTINE FILEIO (SOURCE, DEST)

      CHARACTER*1 A                  ! Define space
      CHARACTER*15 SOURCE            ! Source filename
      CHARACTER*15 DEST              ! Destination filename

      DATA A/' '/

      WRITE (5,1) (A, I=1,2)
1     FORMAT (A)
      TYPE *, 'What is the source filename?'
      READ (5, 3) SOURCE
3     FORMAT (A15)
      WRITE (5,1) A
      TYPE *, 'What is the destination filename?'
      READ (5,3) DEST
      WRITE (5,1) (A, I=1,3)
      RETURN
      END

*************************
*     SUBROUTINE CALIB *
*************************
*     This subroutine calculates k and c, the tof calibration
*     parameters.

      SUBROUTINE CALIB (SOURCE, DEST, K, C, A2)

      DIMENSION TIME(20)
      DIMENSION M(3)
      DIMENSION TAVE(3)
      DIMENSION FUN(3)
```

```
      REAL*4 TIME                ! Ion flight-time
      REAL*4 M                   ! Ion mass to charge ratio
      REAL*4 C                   ! Intercept
      REAL*4 K                   ! Slope
      REAL*4 SUMTIM                    ! Flight-time sum
      REAL*4 TAVE                ! Flight-time mean
      REAL*4 FUN                 ! Function
      REAL*4 KSUM                      ! Sum of the slopes
      REAL*4 CSUM                      ! Sum of the intercepts

      CHARACTER*15 SOURCE              ! Source filename
      CHARACTER*15 DEST                ! Destination
      CHARACTER*1 A                    ! Space
      CHARACTER*1 ANS                  ! Correction response
      CHARACTER*1 A2                   ! File response

      DATA A/' '/                ! Define space

      TYPE *, 'This subroutine calibrates the input data.'
      WRITE (5,10) (A, I=1,2)
10    FORMAT (A)

      IF (A2 .EQ. 'F') CALL FILCAL (SOURCE, K, C)
      IF (A2 .EQ. 'F') RETURN

*     Input masses and flight-times for standards
      DO 100 I=1,3
            SUMTIM=0.0           ! initiate SUMTIM
            TYPE *, 'What is mass number ', I, '?'
            ACCEPT *, M(I)
                  DO 50 J=1,20
                        TYPE *, 'What is the flight time?'
                        READ (5, 20) TIME(J)
                        IF (TIME(J) .LT. 0.0) GO TO 70
                        ! Negative values end data collection
20                      FORMAT (E15.6)
50                CONTINUE

*     Correct input values
70          WRITE (5,10) (A, L=1,3)
            TYPE *,'The values input for mass ',M(I),'are:'
            DO 75 L=1,J-1
                  TYPE *,L,TIME(L)
75          CONTINUE
            TYPE *, 'Are there any corrections?'
            ACCEPT *,ANS
            IF (ANS .EQ. 'y') ANS = 'Y'
            IF (ANS .EQ. 'Y') THEN
                  TYPE *,'Which value needs to be changed?'
                  ACCEPT *, L
                  TYPE *, 'What is the correct flight-time?'
                  ACCEPT *, TIME(L)
                  GO TO 70
            ENDIF
```

```
*       Calculate mean flight-time
              DO 80 L=1,J-1
                    SUMTIM = TIME(L) + SUMTIM
80            CONTINUE
              TAVE(I)=SUMTIM/(J-1)
              WRITE (5,10) (A, L=1,3)
100     CONTINUE

*       CALCULATE K
        KSUM=0.0
        DO 200 I=2,4
              N=I-1
              IF (N .EQ. 3) THEN
                    FUN(I-1)=(TAVE(N)-TAVE(1))/(SQRT(M(N))-
        1                   SQRT(M(1)))
              ELSE
                    FUN(I-1)=(TAVE(I)-TAVE(N))/(SQRT(M(I))-
                          SQRT(M(N)))
              END IF
              KSUM = KSUM + FUN(I-1)
200     CONTINUE
        K=KSUM/3.0

*       CALCULATE C
        CSUM=0.0
        DO 300 I=1,3
              FUN(I)=TAVE(I)-K*SQRT(M(I))
              CSUM=CSUM+FUN(I)
300     CONTINUE
        C=CSUM/3.0

*       PRINT RESULTS
        TYPE *, 'k = ',K, 'C = ',C
        WRITE (5,10) A

*       RETURN TO PROGRAM
        RETURN
        END

****************************
*       SUBROUTINE FILCAL      *
****************************
*       Version: July 3, 1987
*       Edited for new ITR data format: 8/24/88 EDE
*
*       Eric D. Erickson
*
*       PURPOSE:
*       This module permits calibration of the CVC TOFMS using
*       the equation:
*             tof = k * sqrt(m/z) + C
*       This module operates on files imported to it from the
*       main program. The operator inputs the masses and
```

```
*       flight-times of three known ions and the program then
*       calculates mean values for k and C.  A sample standard
*       deviation of each is also calculated.

        SUBROUTINE FILCAL (SOURCE, K, C)

        DIMENSION MASS(3)
        DIMENSION TAVE(3)
        DIMENSION FUN(3)
        DIMENSION TTIM(3)
        DIMENSION SUMTIM(3)
        DIMENSION N2(3)

        CHARACTER*1 A                           ! Space
        CHARACTER*15 SOURCE                     ! Source filename

        INTEGER N2          ! Number of times in ith average
        INTEGER N3                  ! Total number of times in ave

        REAL*4 K                                ! Slope
        REAL*4 C                                ! Intercept
        REAL*4 TTIM                             ! True flight-time
        REAL*4 TIME                             ! Flight-time
        REAL*4 MASS                 ! Ion mass to charge ratio
        REAL*4 TAVE                             ! Mean flight-time
        REAL*4 FUN                              ! Function
        REAL*4 SUMTIM                                   ! Sum of flight-times
        REAL*4 KSUM                                     ! Sum of slopes
        REAL*4 CSUM                                     ! Sum of intercepts
        REAL*4 SDK                              ! Standard deviation of k
        REAL*4 SDC                              ! Standard deviation of C
        REAL*4 TOT                              ! Std dev precursor

        CHARACTER*50 TEXT
        INTEGER*4 INT

        DATA A/' '/

*       Input m/z values and approximate times
        DO 20 I=1,3
                WRITE (5,10) (A, J=1,2)
10              FORMAT (A)
                TYPE *, 'What is the mass of ion number ',I, '?'
                ACCEPT *, MASS(I)
                TYPE *, 'What is the approximate flight-time?'
                ACCEPT *, TTIM(I)
20      CONTINUE

*       Read file for flight-times
        OPEN (UNIT=1, NAME=SOURCE, READONLY, STATUS='OLD',
        1       DISP='SAVE')
        DO 25 I=1,3
                SUMTIM(I)=0.0
                N2(I)=0
```

```
25      CONTINUE
        DO 100 J=1,10000
              READ (1,30, END=110) TEXT
30            FORMAT (A30)
              DECODE (20, 35, TEXT) TIME
35            FORMAT (10X, F10.3)
              DECODE (30, 40, TEXT) INT
40            FORMAT (23X, I7)
              IF (INT .LT. 50) GOTO 100     ! Weed out noise
              IF (ABS(TIME-TTIM(1)) .LT. 0.015) THEN
                    SUMTIM(1) = SUMTIM(1) + TIME
                    N2(1)=N2(1)+1
              ELSE IF (ABS(TIME-TTIM(2)) .LT. 0.015) THEN
                    SUMTIM(2) = SUMTIM(2) + TIME
                    N2(2)=N2(2)+1
              ELSE IF (ABS(TIME-TTIM(3)) .LT. 0.015) THEN
                    SUMTIM(3) = SUMTIM(3) + TIME
                    N2(3)=N2(3)+1
              END IF
100     CONTINUE

*       Calculate mean flight-time
110     DO 120 I=1,3
              TAVE(I) = SUMTIM(I)/N2(I)
120     CONTINUE
        CLOSE (1, DISP='SAVE')                      ! Close file

*       Calculate k
        KSUM = 0.0
        DO 300 I=2,4
              N=I-1
              IF (N .EQ. 3) THEN
                    FUN(I-1)=(TAVE(N)-TAVE(1))/(SQRT(MASS(N))-
                          SQRT(MASS(1)))
              ELSE
                    FUN(I-1)=(TAVE(I)-TAVE(N))/(SQRT(MASS(I))-
                          SQRT(MASS(N)))
              END IF
              KSUM = KSUM + (FUN(I-1) * N2(I-1))
300     CONTINUE
        K=KSUM/(N2(1) + N2(2) + N2(3))
        TOT=0.0
        DO 350 I=1,3
              TOT=TOT + ABS((FUN(I)-K)*N2(I))
              N3=N3 + N2(I)
350     CONTINUE
        SDK=SQRT(TOT/(N3-1))

*       Calculate C
        CSUM=0.0
        DO 400 I=1,3
              FUN(I)=TAVE(I)-K*SQRT(MASS(I))
              CSUM=CSUM+(FUN(I)*N2(I))
400     CONTINUE
```

```
      C=CSUM/N3
      TOT = 0.0
      DO 450 I=1,3
            TOT=TOT + ABS((FUN(I)-C)*N2(I))
450   CONTINUE
      SDC=SQRT(TOT/(N3-1))

*     Print results to the screen
      WRITE (5,500) K,SDK,C,SDC
500   FORMAT (' K= ',F6.3,3X,' SDK= ',F6.3,3X,' C=
            ',F6.3,3X,' SDC=',F6.3)
      RETURN
      END

*************************
*     SUBROUTINE FILDAT      *
*************************
*     Version: July 3, 1987
*
*     Eric D. Erickson
*
*     PURPOSE:
*     This program converts time/intensity data to
*     mass/relative intensity data for the CVC TOFMS. The
*     results are printed to file DEST. Required inputs are
*     the I/O filenames, and the values of the slope and
*     intercept for the time conversion to mass.
*
*     This program has been modified to incorporate changes
*     in ITR data format. The new format has 10 digits for
*     each of the scan number, flight-time, and intensity
*     respectively. - EDE 8/24/88

      SUBROUTINE FILDAT (SOURCE, DEST, K, C)

      REAL*4 K                        ! Slope
      REAL*4 C                        ! Intercept
      REAL*4 M(200)                         ! Mass of the ion
      REAL*4 TOF(200)                       ! Flight time

      INTEGER SCAN                          ! Scan number counter
      INTEGER*4 INTEN(200)                  ! Ion intensity
      INTEGER*4 IMAX                        ! Max ion intensity
      INTEGER SCN(200)                ! Scan number
      INTEGER MA                      ! FRACTIONAL MASS
      INTEGER I,II,N

      CHARACTER*15 SOURCE                   ! Source filename
      CHARACTER*15 DEST                     ! Destination filename
      CHARACTER*60 TEXT                     ! File contents
      CHARACTER*15 MSG(200)   ! Error in data calibration
```

```
      OPEN (UNIT=1, FILE=SOURCE, READONLY, STATUS='OLD',
     1      DISP='SAVE')
                                          ! Open source file
      OPEN (UNIT=2, FILE=DEST, STATUS='NEW', DISP='SAVE')
                                          ! Open destination file
      L = 0
      SCAN = 0
      IMAX = 0
      DO 100 I=1,10000
            L = L + 1
            READ (1, 10, END=110) TEXT! Read line as text
10          FORMAT (A30)
            DECODE (10, 25, TEXT) SCN(L)
25          FORMAT (6X, I4)
            IF (SCN(L) .EQ. 0) GOTO 100 ! Ignore blanks
            DECODE (20, 26, TEXT) TOF(L)
26          FORMAT (10X, F10.3)
            M(L) = ((TOF(L) - C)/K)**2      ! Calculate mass
*     Determine if mass is within reasonable calibration
            MA = M(L)
            X = ABS(M(L) - MA)
            IF (X .GT. 0.15 .AND. X .LT. 0.85) THEN
                  MSG(L) = ' Out of range'
            ELSE
                  MSG(L) = '  '
            ENDIF
            DECODE (30, 28, TEXT) INTEN(L)
28          FORMAT (24X, I6)
            IF (SCN(L) .NE. SCAN) THEN
              II = 0
              DO 150 N = 1,L-1
                IF (II .EQ. 1) THEN
                    II = 0
                    GOTO 150
                ENDIF
                IF (N+1 .LT. L) THEN
                    IF (M(N+1)-(N) .LE. 0.3) THEN
                      IF (INTEN(N) .LT. INTEN(N+1)) GOTO 150
                      IF (INTEN(N) .GT. INTEN(N+1)) II = 1
                    ENDIF
                ENDIF
                WRITE(2,140) SCN(N), TOF(N), M(N), INTEN(N),
     1                    100.*FLOAT(INTEN(N))/FLOAT(IMAX),MSG(N)
140             FORMAT (I7,2X,F6.3,2X,F5.1,2X,
     1                    I7,2X,F7.2,2X,A15)
150           CONTINUE
              SCAN = SCN(L)
              SCN(1) = SCN(L)
              INTEN(1) = INTEN(L)
              MSG(1) = MSG(L)
              TOF(1) = TOF(L)
              M(1) = M(L)
              L = 1
              TYPE *,'WORKING ON SCAN ',SCAN
```

```
            IMAX = INTEN(1)
          ELSE
            IF (IMAX .LT. INTEN(L)) IMAX = INTEN(L)
          ENDIF
100     CONTINUE
110     CLOSE (1, DISP='SAVE')                          ! Close source file
        DO 350 N = 1,L
           WRITE (2, 140) SCN(N),TOF(N),M(N),INTEN(N),
        1               100.*FLOAT(INTEN(N))/FLOAT(IMAX),MSG(N)
350     CONTINUE
        CLOSE (2, DISP='SAVE')

        RETURN

        END
```

Appendix III:

Programs Used for the Degree of Fragmentation Algorithm

APPENDIX III

PROGRAMS USED FOR THE DEGREE-OF-FRAGMENTATION ALGORITHM

This appendix contains the algorithms used to generate degree of fragmentation reconstructed chromatograms.

```
/*      GCSIM.C
**      Eric D. Erickson
**      7/3/89
**
**      C version of GCSIM. Program to produce TII, DIFF, GS,
**      NP, and reconstructed mass chromatogram plot files.
**      This version uses CRICKET GRAPH output format. This
**      version was written to get around formatting problems
**      with data reduced on the ITR which were constantly
**      seen when using the FORTRAN version of this program.
**      A C version of CVCMASS (MASCAL.C) was written also and
**      this program has only been tested with output from that
**      version. I am not sure how this program will handle
**      the different tags used in the two calibration
**      programs. The tags in the C version of the calibration
**      program are "Good Calib" and "Bad Calib". Other than
**      this glitch, the output should be compatible between
**      the two programs.
*/

#include <stdio.h>
#include <math.h>

main()
        {
        char source[20],        /* Source filename      */
           dest[20],            /* Destination filename */
           text1[10],           /* good and bad markers */
           text2[10];           /* good and bad markers */
```

```
        FILE *fp1,*fp2;                 /* File pointers */

        float rithr,                    /* Relative intensity threshold */
            ibase[2000],                /* Intensity of the basepeak */
            tii[2000],    /* Total ion intensity */
            intmas[2000],               /* Intensity for selected mass */
            rint,                       /* Real intensity */
            tmp,                        /* temporary variable */
            gensig[2000],               /* Generic Sigma value */
            gslo,                       /* Minimum generic sigma value */
            gshi,                       /* Maximum generic sigma value */
            mass,                       /* m/z ratio */
            srchm,                      /* search mass */
            delay,                      /* Chromatographic delay time */
            time,                       /* Chromatographic elution time */
            rate,                       /* Spectral generation rate */
            nprat[2000],                /* Number of peaks ratio */
            relint;                     /* Relative intensity */

        long int inten;                 /* Intensity */

        int i;                          /* counters */
        int diff[2000],                 /* Difference plot data */
          scan1,                        /* Previous scan */
          scan,           /* current scan number */
          numpk[2000],                  /* Number of peaks */
          npk25[2000],/* Number of peaks >= 25% base peak */
          numplo,                       /* Minimum number of peaks */
          numphi;                       /* Maximum number of peaks */

/* Query for needed information */

        printf("What is the source filename?\n");
        gets(source);
        fp1 = fopen(source, "r");
        printf("What is the destination filename?\n");
        gets(dest);
        fp2 = fopen(dest, "w");
        printf("What is the chromatographic delay time?");
        printf(" (sec)\n");
        scanf("%f", &delay);
        printf("What is the mass spectral generation rate?");
        printf(" (spectra/sec)\n");
        scanf("%f", &rate);
        printf("What is the desired relative intensity");
        printf(" threshold? (Percent)\n");
        scanf("%f", &rithr);
        printf("Which mass would you like to search for?\n");
        printf("\tEnter 0.0 to skip this search\n");
        scanf("%f", &srchm);
        printf("What is the minimum acceptable value for ");
        printf("generic sigma? (Percent)\n\tEnter a ");
        printf("negative value to skip this calculation.\n");
```

```
        scanf("%f", &gslo);
        if (gslo >= 0.0)
                {
                printf("What is the maximum acceptable value ");
                printf("for generic sigma? (Percent)\n");
                scanf("%f", &gshi);
                }
        printf("What is the minimum number of acceptable ");
        printf("peaks?\n\tEnter a negative value to skip ");
        printf("this calculation.\n");
        scanf("%d", &numplo);
        if (numplo >= 0)
                {
                printf("What is the maximum acceptable number");
                printf(" of peaks?\n");
                scanf("%d", &numphi);
                }
        printf("\n\nStarting data reduction.\n");

/* initialize variables */

        scan1 = 0;
        for (i=0; i<2000; i++)
                {
                diff[i] = 0;
                intmas[i] = 0.0;
                ibase[i] = 0.0;
                gensig[i] = 0.0;
                tii[i] = 0.0;
                numpk[i] = 0.0;
                npk25[i] = 0;
                }

/* read data */

        while ((fscanf(fp1,"%d%f%f%d%f%s%s", &scan, &tmp,
                &mass, &inten, &relint, &text1, &text2)) != EOF)
                {
                if (scan != scan1)
                        {
                        printf("Processing scan #%d\n", scan);
                        scan1 = scan;
                        }
                rint = (float)inten;
                if (diff[scan] < inten)
                        {
                        diff[scan] = inten-
                                (0.01*rithr*((float)inten));
                        }
                if (fabs(mass-srchm) < 0.1)
                        intmas[scan] = rint;
                if (relint > rithr)
                        {
                        tii[scan] += rint;
```

```
                        if (ibase[scan] < rint)
                                ibase[scan] = rint;
                        numpk[scan]++;
                        if (relint > 25.) npk25[scan]++;
                        }
                }

/* calculate ratios */

        for (i=0; i<scan; i++)
                {
/* correct for division by 0 */
                if (tii[i] == 0.0)
                        {
                        gensig[i] = 100.;
                        nprat[i] = 1.;
                        }
/* calculate the value of generic sigma and
** number of peaks ratio */
                else
                        {
                        gensig[i] = 100. * ibase[i] / tii[i];
                        nprat[i] = 100 * ((float)npk25[i]) /
                                ((float)numpk[i]);
                        }
                }
        close(fp1);

/* print out results */
        fprintf(fp2,"*\nscan\ttime\t");
        fprintf(fp2,"tii\t");
        fprintf(fp2,"diff\t");
        if (srchm != 0.0) fprintf(fp2,"mass\t");
        if (gslo >= 0.0)
                {
                fprintf(fp2,"gsig1\t");
                fprintf(fp2,"gsig2\t");
                }
        if (numplo > 0)
                {
                fprintf(fp2,"np5\t");
                fprintf(fp2,"npti\t");
                fprintf(fp2,"np25\t");
                fprintf(fp2,"inprat\t");
                fprintf(fp2,"nprat\n");
                }
        for (i=0; i<scan; i++)
                {
                time = delay + (((float)i)/rate) + 1./(2.*rate);
                fprintf(fp2," %d\t%f\t", i, time);
                fprintf(fp2," %f\t", tii[i]);
                fprintf(fp2," %d\t", diff[i]);
                if (srchm != 0.0)
                        {
```

```
                fprintf(fp2," %f\t", intmas[i]);
                }
        if (gslo >= 0.0)
                {
                if (gensig[i] == 100.)
                        {
                        fprintf(fp2," \t\t");
                        }
                else
                        {
                        fprintf(fp2," %f\t", gensig[i]);
                        if ((gensig[i]>=gslo)&&
                                (gensig[i]<=gshi))
                                {
                                fprintf(fp2," %f\t", tii[i]);
                                }
                        else
                                {
                                fprintf(fp2, " 0.0\t");
                                }
                        }
                }
        if (numplo > 0)
                {
                fprintf(fp2," %d\t", numpk[i]);
                if ((numpk[i]<=numphi)&&(numpk[i]>=numplo))
                        {
                        fprintf(fp2," %f\t", tii[i]);
                        }
                else
                        {
                        fprintf(fp2," 0.0\t");
                        }
                fprintf(fp2," %d\t", npk25[i]);
                if (nprat[i] == 1)
                        {
                        fprintf(fp2," \t \n");
                        }
                else
                        {
                        fprintf(fp2," %f\t", 10000./nprat[i]);
                        fprintf(fp2," %f\n", nprat[i]);
                        }
                }
        }
close(fp2);
printf("Your data have been stored in %s.\n", dest);
}
```

Appendix IV:

Degree of Fragmentation Database

APPENDIX IV

DEGREE OF FRAGMENTATION DATABASE

Symbols used in the following tabulation include:

C The number of carbon atoms in the molecule.

Σ_g Generic sigma value calculated as the base peak intensity divided by the total ion intensity expressed as a percentage.

NP5 The number of peaks in the spectrum with intensities greater than 5% of the base peak intensity.

NP25 The number of peaks in the spectrum with intensities greater than 25% of the base peak intensity.

R The ratio of NP25:NP5 expressed as a percentage.

C	Σ_g	N25	N5	R	Compound
0	27.6	5	13	38.5	Phosphorous Oxychloride
0	28.5	5	11	45.5	Chlorodifluoroamine
0	30.3	4	8	50.0	Sulfur Dichloride
0	32.0	6	8	75.0	Hydrazine
0	33.0	5	7	71.4	Hydrogen Bromide
0	35.4	2	10	20.0	Sulfuryl Chloride Fluoride
0	35.5	4	9	44.4	Phosphorous Oxychloro Difluoride
0	37.2	3	6	50.0	Sulfuryl Fluoride
0	37.7	3	5	60.0	trans-Difluorodiazine
0	40.0	4	5	80.0	Silane
0	41.2	3	6	50.0	Difluoroamine
0	42.6	4	6	66.7	Hydrozoic Acid
0	45.3	2	3	66.7	Phosphorous Oxifluoride
0	46.2	2	4	50.0	Thionyl Fluoride
0	46.2	3	4	75.0	Oxygen Difluoride
0	50.3	5	6	83.3	Hydrogen Sulfide
0	52.6	2	6	33.3	Sulfur Tetrafluoride
0	52.6	2	3	66.7	Ammonia
0	53.6	3	5	60.0	Nitrogen Trifluoride
0	55.4	3	4	75.0	Phosphine
0	56.8	2	5	40.0	cis-Difluorodiazine
0	58.9	2	4	50.0	Tetrafluorohydrazine
0	57.2	3	5	60.0	Sulfur Dioxide
0	59.2	2	4	50.0	Nitrogen Dioxide
0	60.9	1	2	50.0	Silicon Tetrafluoride
0	62.5	1	5	20.0	Nitrous Oxide
0	64.6	1	4	25.0	Sulfur Hexafluoride
0	64.6	3	4	75.0	Hydrogen Chloride
0	65.5	1	4	25.0	Sulfur Oxytetrafluoride
0	76.3	1	2	50.0	Air
0	81.4	1	2	50.0	Water
0	89.3	1	2	50.0	Nitric Oxide
0	95.3	1	1	100.0	Nitrogen
1	23.9	4	11	36.4	Trifluoromethanethiol
1	24.1	4	11	36.4	Chlorobromomethane
1	24.6	6	9	66.7	Carbon Tetrachloride
1	25.3	4	7	57.1	Formic Acid
1	27.0	3	10	30.0	Methyl Bromide
1	29.2	3	6	50.0	Ammonium Carbamate
1	30.1	5	8	62.5	Trifluoromethyl-iminosulfurdifluoride
1	30.9	2	8	25.0	Carbonyl Fluoride
1	31.1	3	11	27.3	Trifluoromethanesulfenyl Chloride
1	31.6	4	9	44.4	Formamide
1	32.0	2	9	22.2	Methyl Mercaptan
1	32.1	4	8	50.0	Dichloromethane
1	32.4	2	13	15.4	Bromodichloromethane
1	32.6	4	10	40.0	Nitromethane
1	35.3	2	12	16.7	Difluorochlorobromo-methane
1	35.3	2	6	33.3	Bromofluoromethane
1	35.3	3	8	37.5	Methyl-N,N-Difluoroamine
1	35.5	5	5	100.0	Methylamine
1	35.8	2	5	40.0	Cyanogen Bromide
1	36.2	2	7	28.6	Chloroform
1	36.4	3	11	27.3	Chlorofluoromethane
1	37.2	2	5	40.0	Difluoromethane
1	38.5	3	3	100.0	Formaldehyde
1	38.9	3	7	42.9	Methylene Chloride
1	39.9	2	11	18.2	Fluorochlorobromomethane
1	40.3	1	10	10.0	Difluorobromomethane
1	40.6	3	5	60.0	Trifluoromethane
1	41.2	3	7	42.9	Carbonyl Chloride Fluoride
1	41.3	3	5	60.0	Methanol
1	41.7	4	5	80.0	Carbonyl Chloride
1	42.3	2	5	40.0	Trichlorofluoromethane
1	45.8	2	5	40.0	Fluoromethane
1	49.3	3	4	75.0	Methane
1	49.5	2	5	40.0	Dichlorodifluoromethane
1	50.0	2	6	33.3	Dichlorofluoromethane
1	50.3	2	7	28.6	Trifluoromethylsulfur Trifluoride
1	52.3	2	7	28.6	Carbonyl Sulfide
1	54.4	2	4	50.0	Methyl Nitrite
1	54.7	2	4	50.0	Cyanogen Chloride
1	55.1	2	5	40.0	Methyl Nitrite
1	56.5	1	7	14.3	Bromotrifluoromethane
1	57.4	2	4	50.0	Iodomethane
1	58.9	1	6	16.7	Chlorodifluoromethane
1	64.9	1	6	16.7	Carbon Disulfide
1	69.4	1	5	20.0	Chlorotrifluoromethane
1	76.8	1	3	33.3	Tetrafluoromethane
1	79.0	1	2	50.0	Hydrogen Cyanide
1	80.3	1	4	25.0	Carbon Dioxide
1	92.0	1	1	100.0	Carbon Monoxide
2	12.4	2	8	25.0	Acetyl Bromide
2	12.7	7	17	41.2	Dichloroacetic Acid
2	13.0	9	25	36.0	1,1,2-Trichloroethane
2	13.9	7	18	38.9	1,1-Dimethylhydrazine
2	14.5	9	23	39.1	Ethanedithiol
2	15.1	7	17	41.2	2-Chloro-1,1,2,2-Tetrafluoroethane
2	15.9	8	18	44.4	Trichloroethylene
2	16.4	8	23	34.8	Dichloroacetyl Chloride
2	16.5	6	20	30.0	2-Mercaptoethanol
2	17.1	6	16	37.5	Ethanethiol
2	17.4	6	20	30.0	Chloral
2	17.4	7	19	36.8	Bromoacetic Acid
2	17.7	4	25	16.0	Dimethylsulfone
2	17.9	5	17	29.4	Chlorodifluoroacetic Acid
2	17.9	5	11	45.5	Tetrachloroethylene
2	17.9	7	14	50.0	Methyl Sulfate
2	18.3	6	11	54.5	Chloroethane
2	18.6	6	11	54.5	Methyl Carbamate
2	19.1	7	15	46.7	Chloromethyl Dichloromethyl Ether
2	19.6	7	12	58.3	sym-Dimethylhydrazine
2	19.9	5	18	27.8	2-Bromoethanol
2	20.0	6	14	42.9	Acetamide
2	20.1	4	16	25.0	1,2-Dichloro-1,2-Difluoroethylene
2	20.4	5	11	45.5	Trichlorofluoroethylene
2	20.5	5	8	62.5	Glyconitrile
2	20.7	5	18	27.8	Chloroacetaldehyde
2	20.8	7	18	38.9	1,1,1,2-Tetrafluoroethane
2	21.0	5	15	33.3	Methylthiocyanate
2	21.3	5	17	29.4	Chloroacetonitrile
2	21.4	4	22	18.2	Ethylene Bromohydrin
2	21.5	2	24	8.3	1,1,2-Trichloro-2-Fluoroethane
2	21.8	6	10	60.0	2-Thiapropane
2	22.1	6	11	54.5	Acetic Acid
2	22.5	5	14	35.7	Fluoroacetic Acid
2	22.6	6	14	42.9	Dichloroacetylene
2	22.6	6	11	54.5	Dimethyl Sulfide
2	22.7	5	19	26.3	1,2-Dichloro-1-Fluoroethane
2	23.5	4	10	40.0	Diazoethane
2	23.6	4	16	25.0	Chloroacetylchloride
2	24.3	5	12	41.7	1,2-Dichloroethane
2	24.6	3	9	33.3	1,1-Dichloro-1-Nitroethane
2	24.6	5	7	71.4	Bromoethane
2	24.7	4	13	30.8	2,3,4-Trithiapentane
2	24.9	5	12	41.7	4-Amino-1,2,4-Triazole
2	25.1	5	12	41.7	Chloropentafluoroethane
2	25.2	3	11	27.3	1,1,1-Trichloroethane
2	25.2	8	25	32.0	Dimethyl Sulfoxide
2	25.3	4	9	44.4	1,2-Dichloroethylene

C	Σg	N25	N5	R	Compound
2	25.6	5	12	41.7	1-Chloro-1,2,2-Trifluoroethylene
2	25.6	5	11	45.5	2,3-Dithiabutane
2	25.8	5	11	45.5	Vinyl Fluoride
2	26.0	5	10	50.0	1,1-Difluoroethane
2	26.5	4	9	44.4	Trifluoroethylene
2	26.9	4	13	30.8	Trichloroacetic Acid
2	27.0	3	9	33.3	Trifluoroacetic Acid
2	27.0	4	11	36.4	Ethylene Imine
2	27.4	4	12	33.3	1,1,1-Trifluoro-2-Chloroethane
2	27.6	4	9	44.4	Dimethyl Peroxide
2	28.1	2	12	16.7	1,1-Dichloro-2,2-Difluoroethane
2	28.4	4	14	28.6	2-Mercaptoethanoic Acid
2	28.8	3	12	25.0	Dimethylamine
2	29.1	4	9	44.4	Ethylene Oxide
2	29.9	2	11	18.2	Bromo-1,2-Difluoroethylene
2	30.0	3	9	33.3	Dichlorodimethylsilane
2	30.3	3	10	30.0	1,1-Dichloro-2,2-Difluoroethylene
2	30.3	4	8	50.0	1,1-Dichloroethylene
2	30.5	3	7	42.9	1-Chloro-2-Fluoroethylene
2	31.1	2	12	16.7	Ethanolamine
2	31.3	3	10	30.0	1,1-Dichloroethane
2	31.4	4	10	40.0	Vinylidine Chloride
2	31.7	4	8	50.0	1-Chloro-2-Bromoethane
2	31.9	4	7	57.1	Ethyl Iodide
2	32.4	3	13	23.1	Methyl-i-Thiocyanate
2	32.8	3	10	30.0	1,2-Dichloro-1,1-Difluoroethane
2	33.1	3	14	21.4	1-Chloro-1,2-Difluoroethylene
2	33.1	3	8	37.5	Iodoacetylene
2	33.1	4	7	57.1	1,1-Chlorofluoroethylene
2	33.7	3	8	37.5	Ethyl-N,N-Difluoroamine
2	34.6	3	9	33.3	Ketene
2	34.8	3	10	30.0	Clorodifluoroacetaldehyde
2	34.9	2	10	20.0	1,1-Dichloro-2,2,2-Trifluoroethane
2	35.3	2	9	22.2	Acetyl Chloride
2	35.6	2	8	25.0	Nitroethane
2	35.9	2	6	33.3	Glycolic Acid
2	36.2	3	8	37.5	Ethyl Nitrate
2	36.3	3	7	42.9	Dimethyl Sulfite
2	37.2	4	5	80.0	Tetrafluoroethylene
2	37.4	2	9	22.2	Trichloroacetonitrile
2	37.4	3	5	60.0	Ethanal
2	37.9	2	11	18.2	Ethylamine
2	37.9	3	7	42.9	Chloroacetic Acid
2	38.7	4	6	66.7	Methyl Formate
2	39.1	3	11	27.3	Chloroacetylene
2	39.7	5	8	62.5	Vinyl Chloride
2	39.9	2	10	20.0	1-Chloro-2,2-Difluoroethylene
2	40.3	3	9	33.3	Fluoroethane
2	40.4	3	6	50.0	Chloromethyl Ether
2	40.9	3	7	42.9	Glycerolaldehyde
2	41.1	1	10	10.0	Chloral Hydrate
2	41.1	2	7	28.6	Ethanol
2	41.2	3	8	37.5	Oxalyl Chloride
2	41.2	3	7	42.9	Azomethane
2	41.3	4	6	66.7	1,2-Difluoroethane
2	41.4	3	5	60.0	Ethylene
2	41.6	3	6	50.0	Vinyl Bromide
2	41.9	4	7	57.1	Dimethyl Ether
2	42.3	2	7	28.6	Trifluoroacetonitrile
2	42.6	3	5	60.0	Bis Chloromethyl Ether
2	42.8	1	7	14.3	2,2,2-Trifluoroethanol
2	43.0	3	5	60.0	Diclorofluoroethylene
2	43.2	2	5	40.0	1-Bromo-2-Chloroethylene
2	45.2	2	7	28.6	Acetonitrile
2	45.6	1	7	14.3	2,2,2-Trichloroethanol
2	46.6	2	8	25.0	Ethylene Glycol
2	46.7	3	5	60.0	Ethane
2	46.8	2	6	33.3	1,1-Chlorofluoroethane
2	48.2	2	6	33.3	Methyl Chloroformate
2	48.6	1	7	14.3	Glyoxal
2	49.6	2	6	33.3	Oxalic Acid
2	50.6	1	7	14.3	2-Fluoroethanol
2	52.1	1	4	25.0	1,1,1-Trifluoroethane
2	56.6	2	4	50.0	Hexafluoroethane
2	56.9	1	6	16.7	Fluoroacetylene
2	58.4	1	4	25.0	1,2-Ethanediamine
2	58.5	2	5	40.0	Ethanesulfonylfluoride
2	58.8	1	5	20.0	2-Chloroethanol
2	62.6	1	3	33.3	Dichlorfluoroacetonitrile
2	66.4	1	5	20.0	Chlorodifluoroacetonitrile
2	76.6	1	3	33.3	Acetylene
3	10.2	12	32	37.5	1,1,1-Trifluoro-3-Chloropropane
3	11.8	8	39	20.5	1,1,1-Trichloropropanone
3	12.9	8	27	29.6	1-Chloro-2-Propanone
3	13.2	12	18	66.7	Methyl Bromoacetate
3	13.3	9	25	36.0	1-Propanethiol
3	13.5	10	22	45.5	Trimethylhydrazine
3	14.2	3	7	42.9	1-Chloro-2-Bromopropane
3	14.2	8	17	47.1	Ethyl Carbamate
3	14.5	8	26	30.8	2,3-Dichloropropionic Acid
3	15.2	7	15	46.7	2-Chloropropionic Acid
3	15.5	9	19	47.4	1,3-Propanedithiol
3	15.8	8	23	34.8	2,3-Dichloroacrylic Acid
3	15.9	6	29	20.7	1,1-Dichloropropanone
3	16.0	5	27	18.5	2,2-Dichloropropionic Acid
3	16.3	7	19	36.8	1,2-Dichloropropane
3	16.5	7	19	36.8	Methyl Chloroacetate
3	16.7	4	22	18.2	1,1-Dichloropropene
3	16.7	7	15	46.7	3,3,3-Trifluoro-1-Propene
3	16.8	6	16	37.5	3-Chloro-1,2-Propanediol
3	16.9	7	17	41.2	Propanoic Acid
3	17.0	5	17	29.4	1,3-Propanediol
3	17.4	7	12	58.3	3-Bromopropionitrile
3	17.5	5	22	22.7	1,2-Dichloropropene
3	17.6	7	19	36.8	Epichlorohydrin
3	18.1	8	16	50.0	1-Chloro-3-Bromopropane
3	18.2	4	22	18.2	1,2,2-Trichloropropene
3	19.2	7	13	53.8	Acrylamide
3	19.4	7	13	53.8	Allyl Alcohol
3	19.8	5	16	31.3	2-Propanethiol
3	20.0	5	21	23.8	1,1-Dichloro-1-Fluoropropane
3	20.3	1	8	12.5	1-Bromo-2-Propanol
3	20.5	5	12	41.7	Vinyl Formate
3	20.6	4	17	23.5	Glycidol
3	20.7	6	13	46.2	Propylene Sulfide
3	20.8	6	15	40.0	Formaldehyde Dimethyl Hydrazone
3	20.9	6	13	46.2	2-Thiobutane
3	21.2	7	11	63.6	Propylene Oxide
3	21.4	6	15	40.0	Imidazole
3	21.4	8	11	72.7	1,2-Epoxypropane
3	21.6	6	18	33.3	1,2,3-Trichloropropane
3	21.8	6	18	33.3	Dichloromalonitrile
3	21.8	6	15	40.0	N,N-Dimethylformamide
3	21.8	6	11	54.5	Dimethyl Carbonate
3	22.2	5	13	38.5	Ethyl i-Thiocyanate
3	22.5	5	18	27.8	2,3-Dichloro-1-Propanol
3	22.5	4	14	28.6	Allylamine
3	22.7	4	14	28.6	1,2,2-Trichloropropane
3	23.0	4	13	30.8	1-Nitropropane
3	23.1	5	14	35.7	Trithiane

C	Σ_g	N25	N5	R	Compound
3	23.2	5	16	31.3	3,3,3-Trifluoro-1,2-Chloropropene
3	23.7	5	8	62.5	Propionaldehyde
3	24.0	4	13	30.8	3-Chloropropanenitrile
3	24.5	6	15	40.0	Glycerol
3	24.8	3	15	20.0	2,3-Dichloropropene
3	24.8	5	10	50.0	Cyclopropane
3	25.0	4	16	25.0	1,2-Dichloro-2-Fluoropropane
3	25.2	5	11	45.5	Acrylic Acid
3	25.3	6	7	85.7	Acrolein
3	25.4	7	10	70.0	n-Propyl Nitrite
3	25.5	7	11	63.6	Propiolactone
3	26.0	5	10	50.0	Hexafluoropropene
3	26.0	6	12	50.0	Ethylene Carbonate
3	26.1	4	9	44.4	Acrylonitrile
3	26.2	4	12	33.3	Ethyl Formate
3	26.3	6	8	75.0	2-Chloroethylchloroformate
3	26.4	5	11	45.5	Carbon Suboxide
3	26.6	2	14	14.3	3,3,3-Trichloropropene
3	26.6	4	12	33.3	1,3-Dichloropropanone
3	26.8	4	11	36.4	Epibromohydrin
3	27.2	4	12	33.3	2-Hydroxypropanenitrile
3	27.4	4	10	40.0	2-Nitropropane
3	27.5	4	11	36.4	1,1,2-Trichloropropane
3	27.6	3	14	21.4	Trichloropropionitrile
3	27.8	4	14	28.6	3-Chloropropionic Acid
3	28.2	4	9	44.4	2,2-Dichloropropane
3	28.2	5	8	62.5	1,3-Dioxylane
3	28.4	3	13	23.1	Chloromethoxy Acetic Acid
3	28.4	3	9	33.3	Propionyl Chloride
3	29.5	4	9	44.4	1,3-Dichloropropene
3	29.6	3	12	25.0	2,2-Dichloropropionyl Chloride
3	29.8	3	10	30.0	3-Chloropropene
3	29.8	3	10	30.0	2-Chloropropene
3	30.2	4	7	57.1	Propanal
3	30.4	3	9	33.3	Pyruvaldehyde
3	30.4	4	11	36.4	Propane
3	30.4	5	8	62.5	Methyl Carbonate
3	30.6	3	14	21.4	Trimethylamine
3	30.7	3	10	30.0	3-Chloroacrylonitrile
3	30.9	3	9	33.3	Propylene
3	31.0	3	9	33.3	Chlorotrimethylsilane
3	31.1	4	8	50.0	Lactic Acid
3	31.2	3	9	33.3	Acrylyl Chloride
3	31.6	3	9	33.3	1-Bromopropane
3	31.9	3	13	23.1	3,3,3-Trifluoropropyne
3	31.9	3	12	25.0	Propionamide
3	32.1	3	11	27.3	2-Fluoropropene
3	32.1	3	9	33.3	1-Chloropropene
3	32.3	3	14	21.4	3-Chloro-1-Propanol
3	32.5	3	9	33.3	1,1,2,2,3-Pentafluoropropane
3	33.0	3	7	42.9	1-Bromo-2-Propyne
3	33.1	3	10	30.0	Allyl Fluoride
3	33.1	4	11	36.4	N-Methylethylenimine
3	33.2	3	12	25.0	Dihydroxy Acetone
3	33.4	3	11	27.3	Pyruvonitrile
3	33.6	2	10	20.0	2-Propyn-1-ol
3	34.2	3	10	30.0	Trimethylene Oxide
3	34.2	4	9	44.4	1-Fluoropropane
3	34.3	3	8	37.5	3,3-Dichloropropene
3	35.0	2	10	20.0	Propylene Glycol
3	35.0	3	8	37.5	1,3-Dichloropropane
3	35.1	2	10	20.0	1-Chloro-2-propanol
3	35.2	2	12	16.7	Trimethylenediamine
3	35.3	2	12	16.7	3,3,3-Trifluoro-1-Chloropropene
3	35.3	2	11	18.2	Ethylene Glycol Monoformate
3	35.3	2	10	20.0	Propargyl Alcohol
3	35.5	3	9	33.3	1-Chloropropane
3	35.8	2	10	20.0	Propanenitrile
3	36.0	3	8	37.5	2-Chloropropane
3	36.5	4	4	100.0	Allene
3	36.6	3	10	30.0	2-Bromopropane
3	37.7	4	7	57.1	Malonic Acid
3	38.0	1	10	10.0	Pyruvic Acid
3	38.0	4	9	44.4	2-Methoxy-1-Ethanol
3	38.5	2	6	33.3	1,3,3-Trifluoro-3-Chloropropene
3	39.3	3	10	30.0	2-Amino-1-Propanol
3	40.1	4	5	80.0	Propyne
3	40.3	2	7	28.6	Thiacyclobutane
3	40.4	3	7	42.9	Methyl Dichloroacetate
3	41.9	3	8	37.5	Propargyl Bromide
3	43.0	3	4	75.0	Vinyl Methyl Ether
3	43.2	2	7	28.6	Propargyl Chloride
3	43.7	3	5	60.0	s-Trioxane
3	43.7	4	5	80.0	Allyl Bromide
3	44.1	3	5	60.0	1,3-Dichloro-2-Propanol
3	44.2	1	8	12.5	1-Amino-2-Propanol
3	44.7	3	4	75.0	Dimethoxymethane
3	44.8	1	9	11.1	1,1,2-Trifluoro-2-Chloroethyl Methyl Ether
3	45.0	3	7	42.9	1,1,1,3,3,3-Hexafluoropropane
3	45.4	2	6	33.3	1,2-Diaminopropane
3	47.8	1	7	14.3	Acetol
3	49.0	2	6	33.3	Methoxyacetic Acid
3	49.4	1	6	16.7	3-Bromo-3,3-Difluoro-1-Propene
3	50.0	1	10	10.0	n-Propanol
3	50.1	2	6	33.3	1,3,5-Trioxane
3	51.0	1	8	12.5	1,2-Propanediol
3	51.4	1	7	14.3	1-Chloro-2,2-Difluoropropane
3	51.6	1	5	20.0	Trimethyl Silanol
3	52.3	1	7	14.3	2-Methoxyethanol
3	52.4	2	5	40.0	2-Fluoropropane
3	53.9	1	7	14.3	i-Propanol
3	55.0	1	6	16.7	Chloroacetone
3	55.5	1	6	16.7	1-Amino-3-Hydroxypropane
3	56.7	2	5	40.0	Acetone
3	57.3	1	3	33.3	Propylenediamine
3	58.4	1	4	25.0	n-Propylamine
3	61.2	1	5	20.0	Hydroxy-2-Propanone
3	63.7	1	5	20.0	Methyl Acetate
3	65.3	2	4	50.0	i-Propylamine
3	66.3	1	3	33.3	2,2-Difluoropropane
4	10.6	11	30	36.7	1,2,3,4-Diepoxybutane
4	11.1	12	24	50.0	3-Methoxypropylamine
4	12.2	9	27	33.3	Butyryl Chloride
4	12.2	10	25	40.0	1,2,4-Butanetriol
4	13.0	7	25	28.0	2-Methyl-2-Propen-1-ol
4	13.0	7	24	29.2	Butyne-1,4-diol
4	13.1	11	21	52.4	Tetramethylammonium Hydroxide
4	13.2	3	17	17.6	1,2-Dichlorobutane
4	13.3	10	26	38.5	2-Methyl-1,3-Thioxalane
4	13.5	9	24	37.5	Diethanolamine
4	13.9	7	22	31.8	2,3-Dichlorobutyric Acid
4	14.2	8	17	47.1	n-Butylnitrate
4	14.4	7	18	38.9	2-Butanethiol
4	14.9	7	23	30.4	2-Butene-1,4-diol
4	15.0	7	22	31.8	1,4-Butanedithiol
4	15.1	8	23	34.8	2,3-Dichloro-2-Butene
4	15.1	8	16	50.0	i-Butyryl Chloride
4	15.3	6	14	42.9	1-Fluorobutane
4	15.3	9	16	56.3	2(2-Chloroethoxy) Ethanol
4	15.4	8	28	28.6	3-Chloropropyl Chloroformate
4	15.4	7	21	33.3	1-Butanethiol

C	Σ_g	N25	N5	R	Compound
4	15.4	7	17	41.2	Diethyl Sulfide
4	15.5	7	14	50.0	2-Chlorobutane
4	15.7	9	17	52.9	2-Methyl-1-Propanethiol
4	16.1	8	24	33.3	Hydroxybuteric Acid
4	16.1	8	22	36.4	Cyclopropyl Carboxylic Acid
4	16.3	6	26	23.1	Methyl 2,3-Dichloropropionate
4	16.4	5	21	23.8	3,4-Dithiahexane
4	16.4	5	21	23.8	1,3-Dichloro-2-Methylpropane
4	16.4	8	14	57.1	Butadiene Dioxide
4	16.5	6	20	30.0	Methyl Vinyl Carbinol
4	16.8	9	21	42.9	Methyl Hydracrylate
4	16.8	7	16	43.8	Crotonic Acid
4	17.0	8	17	47.1	Aldol
4	17.2	3	29	10.3	2-Chlorocrotonaldehyde
4	17.2	6	16	37.5	2,3-Dithiahexane
4	17.3	8	16	50.0	i-Propyl Formate
4	17.4	5	18	27.8	3,4-Dithiahexane
4	17.6	7	14	50.0	n-Butyl Nitrate
4	17.9	5	22	22.7	1,1,3-Trichloro-2-Methylpropene
4	18.2	4	20	20.0	1,3-Butanediol
4	18.2	5	15	33.3	Butenal
4	18.2	7	14	50.0	Allyl Formate
4	18.3	7	17	41.2	2-Ethylethylenimine
4	18.3	7	14	50.0	Butanal
4	18.4	6	15	40.0	2,5-Dihydrofuran
4	18.6	6	14	42.9	Methyl Allyl Ether
4	18.6	7	15	46.7	1-Butanol
4	18.7	8	12	66.7	Morpholine
4	18.8	2	10	20.0	4-Bromobutyronitrile
4	18.8	4	17	23.5	1,4-Dichloro-2-Butene
4	19.0	4	21	19.0	2-Chlorobutyric Acid
4	19.0	5	17	29.4	1,4-Dithian
4	19.1	6	15	40.0	1,4-Butanediol
4	19.3	5	17	29.4	i-Crotonic Acid
4	19.4	4	16	25.0	1,2-Bis(Methyl Mercapto) Ethylene
4	19.5	6	13	46.2	Ethyl Vinyl Ether
4	19.6	5	17	29.4	3-Chloro-2-Methylpropene
4	19.6	5	14	35.7	Dioxane
4	19.7	6	19	31.6	2-Aminopyrimidine
4	19.7	6	17	35.3	Divinyl Sulfide
4	19.8	6	15	40.0	3-Chlorobutyric Acid
4	19.8	6	15	40.0	Dimethoxy Chloroacetal
4	19.9	6	18	33.3	Diethyl Sulfate
4	19.9	6	17	35.3	Vinyl Glycol Ether
4	20.2	4	20	20.0	1,1-Dichlorobutane
4	20.2	5	24	20.8	2,3-Dichloro-1,4-Dioxane
4	20.4	7	15	46.7	Butyrolactone
4	20.5	7	18	38.9	Methyl Mercapto Propionaldehyde
4	20.6	6	21	28.6	2-Buten-1-ol
4	20.7	6	18	33.3	Vinyl-2-Chloroethyl Ether
4	20.8	5	20	25.0	(2-Hydroxyethyl)-Ethyl Sulfide
4	20.8	5	16	31.3	2-Fluoro-1,3-Butadiene
4	21.0	4	16	25.0	Ethoxyacetic Acid
4	21.0	5	18	27.8	3,3,3-Trichloro-2-Methylpropene
4	21.1	4	19	21.1	2,3-Dichloro-2-Methylpropionaldehyde
4	21.1	5	15	33.3	3-Butanoic Acid
4	21.2	5	14	35.7	Butyramide
4	21.3	4	12	33.3	Methyl Vinyl Ketone
4	21.4	6	11	54.5	1,3-Butadiene
4	21.5	4	14	28.6	Trichlorobutane
4	21.5	5	14	35.7	3-Methyl-2-Oxazolidinone
4	21.6	4	19	21.1	Allyl i-Thiocyanate
4	21.7	5	17	29.4	3-Methylpyrazole
4	21.8	7	13	53.8	2-Methyl-1,3-Dioxyacetylpentane
4	22.1	3	16	18.8	2-Methylpropenal
4	22.1	5	14	35.7	Diethylamine
4	22.1	5	14	35.7	Methyl-3-Chloropropionate
4	22.3	6	13	46.2	2-Chloro-1-Methyl Chloroformate
4	22.3	7	12	58.3	cis-2,3-Epoxybutane
4	22.6	4	18	22.2	Tetramethoxysilane
4	22.6	5	15	33.3	Methyl Propyl Sulfide
4	22.7	6	14	42.9	2,3-Dichlorobutane
4	22.8	3	12	25.0	2-Thiophenethiol
4	22.8	5	14	35.7	Tetrahydrothiophene
4	22.8	6	15	40.0	Methyl i-Propenyl Ether
4	23.0	8	14	57.1	Piperazine
4	23.1	6	16	37.5	3-Methoxy-1,2-Propanediol
4	23.3	6	15	40.0	n-Buteric Acid
4	23.4	3	16	18.8	3,4-Dichloro-1-Butene
4	23.4	4	13	30.8	Methyl 2-Chloropropionate
4	23.4	4	13	30.8	Methyl 2,2-Dichloropropionate
4	23.5	6	13	46.2	i-Butylene Oxide
4	23.7	5	13	38.5	Hexafluoro-2-Butyne
4	23.7	6	13	46.2	1-Butyne
4	23.7	6	13	46.2	trans-2,3-Epoxybutane
4	23.9	4	9	44.4	Cyclobutane
4	24.0	4	9	44.4	Bis(2-Chloroethyl) Ether
4	24.1	3	14	21.4	Methacrylic Acid
4	24.1	4	16	25.0	Methyl Cyanoacetate
4	24.2	4	16	25.0	Dichlorotetrahydrofuran
4	24.3	4	14	28.6	1,2-Bis(Methylmercapto) Ethane
4	24.3	5	13	38.5	Acetone Cyanohydrin
4	24.4	5	10	50.0	Ethylene Diformate
4	24.5	4	15	26.7	2-Thiapentane
4	24.7	4	15	26.7	1,4-Thioxane
4	24.8	3	12	25.0	1,1-Dichloro-3-Buten-2-one
4	24.9	7	12	58.3	Acetaldazine
4	25.0	4	10	40.0	Maleic Acid
4	25.2	4	16	25.0	Glycerol Monomethyl Ether
4	25.2	5	9	55.6	1,2-Epoxy-2-Methylpropane
4	25.7	3	14	21.4	1,2-Dichloro-2-Methylpropane
4	25.7	3	13	23.1	2-Amino-4-(Chloromethyl)-Thiazole
4	25.8	4	14	28.6	2-Methoxypropene
4	25.9	5	9	55.6	Pyrrole
4	26.2	3	10	30.0	1,4-Dichloro-2-Butyne
4	26.4	5	11	45.5	Vinylidine Cyanide
4	26.5	5	10	50.0	N,N-Dimethylacetamide
4	26.7	5	13	38.5	Vinyl Acetonitrile
4	26.7	6	12	50.0	1,2-Butadiene
4	26.8	3	15	20.0	Fumaronitrile
4	26.9	2	15	13.3	2,2-Dichloro-4-Hydroxy-butyric Acid Lactone
4	26.9	5	11	45.5	1,1-Dimethoxyethane
4	26.9	6	10	60.0	Dimethylketene
4	27.2	4	14	28.6	2-Bromoethyl Ethyl Ether
4	27.5	4	14	28.6	Ethyl Sulfite
4	27.6	4	13	30.8	Butadiene Monoxide
4	27.6	4	12	33.3	Thiophene
4	27.7	5	12	41.7	2-Butene
4	27.8	3	12	25.0	2-Chloro-1,2-Difluorovinyl Ethyl Ether
4	28.6	4	11	36.4	2-Hydroxy-i-Buteric Acid
4	28.7	4	10	40.0	2-Bromobutane
4	28.9	3	11	27.3	1-Bromo-2-Methylpropane
4	29.1	3	13	23.1	2-Methylpropanenitrile
4	29.1	3	11	27.3	1,2-Butanediol

C	Σ_g	N26	N5	R	Compound
4	29.1	4	12	33.3	Ethylene Cyanide
4	29.1	4	12	33.3	Butanoic Acid
4	29.5	3	15	20.0	1,3-Dichlorobutane
4	29.5	3	12	25.0	1-Chloro-2-Butenol
4	29.7	3	11	27.3	t-Nitrobutane
4	29.9	3	12	25.0	1,1-Bis(Methylmercapto) Methyl Sulfide
4	29.9	4	13	30.8	1-Chlorobutane
4	30.0	3	13	23.1	3-Butyn-2-ol
4	30.0	5	12	41.7	Thiadimethyl Acetal
4	30.3	3	9	33.3	Malic Anhydride
4	30.4	3	9	33.3	2-Chloro-2-Methylpropane
4	30.5	4	10	40.0	1,1-Bis(Methylmercapto) Ethane
4	30.5	4	7	57.1	t-Butylbromide
4	30.6	3	10	30.0	Pyrrolidine
4	30.6	3	9	33.3	Acetoin
4	30.6	4	8	50.0	2-Ethoxyethanol
4	30.7	4	10	40.0	2-Butyne
4	30.9	4	11	36.4	Diethyl Peroxide
4	31.1	2	10	20.0	Methyl Acetyl Carbinol
4	31.2	4	9	44.4	Methylmalonitrile
4	31.4	4	11	36.4	3,4-Epoxy-1-Butene
4	31.6	4	13	30.8	Phthalic Anhydride
4	31.9	5	9	55.6	N-Butane
4	32.1	4	11	36.4	1-Butene
4	32.1	3	8	37.5	Methyl Propionate
4	32.1	4	10	40.0	Methyl i-Propyl Ether
4	32.3	4	6	66.7	Trimethyl o-Formate
4	32.4	2	7	28.6	Diethyl Ether
4	32.6	2	8	25.0	3-Hydroxy-2-Butanone
4	32.7	3	12	25.0	1-Bromobutane
4	32.8	3	11	27.3	1,4-Dioxane
4	33.0	3	10	30.0	2-Methylpropene
4	33.1	3	14	21.4	3-Butyn-1-ol
4	33.2	3	8	37.5	1-Chloro-2-Methylpropane
4	33.7	3	9	33.3	N-Methylol Acrylamide
4	34.1	2	8	25.0	Ethyldifluoroacetate
4	35.0	1	14	7.1	1,4-Dichlorobutane
4	35.1	2	12	16.7	Ethyldimethylamine
4	36.3	3	7	42.9	Succinic Acid
4	36.7	2	10	20.0	Chlorobutyronitrile
4	37.5	2	13	15.4	Diketene
4	37.5	2	11	18.2	Tetramethylenediamine
4	37.6	1	12	8.3	2-Amino-1-Butanol
4	38.0	3	6	50.0	n-Butonitrile
4	38.1	2	7	28.6	Furan
4	38.9	3	6	50.0	1,1,1-Trifluoro-2-Butanone
4	39.2	2	9	22.2	2-Chloromethyl-1,3-Dioxolane
4	39.6	2	5	40.0	Ethyl Trifluoroacetate
4	40.3	2	7	28.6	Perfluorocyclobutene
4	40.4	1	9	11.1	2-Butanol
4	40.8	4	7	57.1	1-Buten-3-yne
4	41.3	2	5	40.0	Succinic Anhydride
4	41.5	2	7	28.6	2-Chloroethyl Acetate
4	41.8	2	9	22.2	Methyl Acrylate
4	42.1	1	9	11.1	sec-Butanol
4	42.4	2	9	22.2	Ethyl Dichloroacetate
4	42.6	1	12	8.3	2-Methyl-2-Amino-1-Propanol
4	43.6	3	10	30.0	Ethylene Glycol
4	45.0	3	5	60.0	2-Methylpropane
4	45.3	1	6	16.7	2-(Dichloromethyl)-1,3-Dioxolane
4	45.4	1	9	11.1	2,3-Butanediol
4	45.6	2	9	22.2	Diethylene Glycol
4	45.6	2	6	33.3	Perfluoro-1,3-Butadiene
4	46.1	1	9	11.1	sec-Butylamine
4	46.3	5	12	41.7	Chloroprene
4	47.4	2	9	22.2	Dicyanoacetylene
4	47.4	2	6	33.3	2-Methoxy-1-Propanol
4	47.8	3	6	50.0	Pyrizine
4	48.0	1	9	11.1	Methyl 2-Hydroxypropionate
4	48.3	1	7	14.3	1-Methoxy-2-Propanol
4	49.0	2	6	33.3	t-Butanol
4	49.3	1	7	14.3	Methyl n-Propyl Ether
4	50.5	1	7	14.3	2-Fluoro-2-Methylpropane
4	50.8	1	9	11.1	2-Hydroxyethyl Acetate
4	51.3	1	5	20.0	Tetramethylsilane
4	51.4	1	10	10.0	Ethyl Acetate
4	53.1	1	6	16.7	Methyl Ethyl Ketone
4	53.4	1	6	16.7	t-Butylamine
4	53.9	1	5	20.0	2,3-Butanedione
4	54.1	3	4	75.0	2-Vinyloxyethanol
4	56.3	2	5	40.0	1,3-Butadiene
4	57.6	1	4	25.0	4-Chloro-4,4-Difluoro-2-Butanone
4	58.0	1	5	20.0	n-Butylamine
4	60.8	1	5	20.0	3-Chloro-2-Butanol
4	63.3	1	4	25.0	Diacetyl
4	64.5	1	4	25.0	2-Chloropropyl Methyl Ether
4	69.8	1	5	20.0	Vinyl Acetate
4	72.9	1	3	33.3	Acetic Anhydride
5	9.5	14	25	56.0	3-Penten-1-ol
5	9.7	13	24	54.2	Valeryl Chloride
5	10.3	10	26	38.5	2-Chloro-2-Methylbutane
5	11.4	13	27	48.1	3-Methylthiacyclopentane
5	11.5	8	29	27.6	1,1-Dichloro-2,2-Dimethylcyclopropane
5	12.5	9	27	33.3	1,3-Bis(Methylmercapto) Propane
5	12.8	9	24	37.5	n-Butyl i-Thiocyanate
5	12.9	9	25	36.0	t-Amyl Chloride
5	13.0	8	19	42.1	1-Chloropentane
5	13.1	10	12	83.3	3-Methyl-1-Butanol
5	13.3	9	25	36.0	Furfuryl Alcohol
5	13.6	7	22	31.8	2-Methyl-3,4-Dithiahexane
5	13.7	11	22	50.0	2-Methyl-1-Butanethiol
5	14.1	9	16	56.3	sec-Amyl Chloride
5	14.2	8	22	36.4	sec-Butyl i-Thiocyanate
5	14.2	10	20	50.0	2-Pentanethiol
5	14.7	9	23	39.1	3-Thiahexane
5	14.8	8	19	42.1	2-Methylpyrrolidone
5	14.8	9	20	45.0	i-Butyl Formate
5	14.9	8	21	38.1	Ethyl 3-Chloropropanoate
5	14.9	7	17	41.2	3-Methylbutanal
5	14.9	9	21	42.9	i-Amyl Nitrate
5	15.1	8	25	32.0	2-Methyl-3-Thiapentane
5	15.1	8	17	47.1	1,4-Pentadiene
5	15.2	8	24	33.3	Dihydropyran
5	15.4	8	25	32.0	Ethyl i-Propyl Sulfide
5	15.4	7	20	35.0	2-Methyl-1,3-Butadiene
5	15.6	8	19	42.1	1,3-Pentadiene
5	15.7	9	17	52.9	Tetrahydropyran
5	15.8	9	23	39.1	Cyclopentanethiol
5	15.8	11	21	52.4	3-Methyl-1-Butanethiol
5	15.9	8	14	57.1	2-Methoxyethyl Ethenyl Ether
5	16.0	9	20	45.0	4-Pentenal
5	16.4	7	18	38.9	3-Furoic Acid
5	16.4	9	16	56.3	4-Methyl-n-Dioxane
5	16.4	8	14	57.1	1-Pentanol
5	16.5	7	17	41.2	3-Chloropentane
5	16.5	8	14	57.1	3-Pentanethiol
5	16.7	5	16	31.3	2-Methylbutanoic Acid
5	16.7	6	16	37.5	Dimethyl Malonate
5	17.4	6	19	31.6	2-Thiahexane
5	17.4	9	19	47.4	3-Methyl-2-Butanethiol
5	17.5	7	18	38.9	1-Pentyne
5	17.6	8	14	57.1	2-Methyl-1-Butanol

C	Σ_g	N25	N5	R	Compound
5	17.7	6	21	28.6	2-Pentyne
5	17.7	7	16	43.8	2-Methyltetrahydrofuran
5	17.7	8	13	61.5	N,N-Diethylformamide
5	17.8	7	16	43.8	Valerolactone
5	17.9	5	20	25.0	3-Methylfuran
5	17.9	8	14	57.1	3-Methylbutyle Nitrite
5	17.9	8	14	57.1	i-Amyl Nitrite
5	18.1	7	14	50.0	2-Methoxyethyl Vinyl Ether
5	18.4	7	22	31.8	2,3-Pentadiene
5	18.6	7	16	43.8	N-Valeraldehyde
5	18.6	8	17	47.1	2-Methyl-2-Butanethiol
5	18.7	7	19	36.8	3-Methyl-1,2-Butadiene
5	19.1	6	20	30.0	3-Methyl-2-Butenal
5	19.1	6	18	33.3	N-Ethylacrylamide
5	19.2	7	13	53.8	i-Valeraldehyde
5	19.4	4	14	28.6	Spiropentane
5	19.4	7	16	43.8	2-Furoic Acid
5	19.5	5	17	29.4	2-Methylfuran
5	19.5	6	16	37.5	4-Hydroxy-2-Pentenoic Acid Lactone
5	19.7	5	21	23.8	3-Ethoxypropionaldehyde
5	19.8	6	16	37.5	i-Valeric Acid
5	19.9	7	18	38.9	N,N-Dimethyl Acrylamide
5	19.9	8	14	57.1	1-Pentanethiol
5	20.0	6	18	33.3	3-Ethoxy-1-Propanol
5	20.1	6	14	42.9	Tetrahydrofurfuryl Alcohol
5	20.2	4	17	23.5	Dimethylmalonitrile
5	20.2	6	12	50.0	2-Chloropentane
5	20.2	7	12	58.3	Piperidine
5	20.3	5	14	35.7	Valeronitrile
5	20.3	5	14	35.7	N-Methylpyrrolidine
5	20.5	6	17	35.3	1,5-Dichloropentane
5	20.6	7	18	38.9	sec-Amyl Nitrate
5	20.7	5	11	45.5	2-Methylbutyraldehyde
5	21.0	6	11	54.5	2-Methylpentane
5	21.1	4	13	30.8	Diethyl Carbonate
5	21.2	6	16	37.5	2,2-Dimethoxypropane
5	21.3	2	7	28.6	Ethyl Lactate
5	21.3	7	14	50.0	1,1-Dimethoxypropane
5	21.5	5	13	38.5	Methylenecyclobutane
5	21.5	6	13	46.2	2,2-Dimethyl-1-Propanethiol
5	21.6	3	22	13.6	3,5-Dimethylpyrrazole
5	21.7	6	19	31.6	Senecioic Acid
5	21.7	5	15	33.3	2-Methyl-1-Buten-3-yne
5	21.8	4	18	22.2	Dimethylpropiolactone
5	21.8	4	15	26.7	Tiglaldehyde
5	21.8	6	14	42.9	1,3-Dioxep-5-ene
5	22.0	4	19	21.1	2-Pentyne
5	22.2	5	19	26.3	N-Methylpyrrole
5	22.3	4	19	21.1	2-Chlorovaleric Acid
5	22.4	5	13	38.5	Diethoxymethane
5	22.5	4	18	22.2	2-Methylthiacyclopentane
5	22.5	5	13	38.5	2-Chloroethyl Propionate
5	22.5	5	11	45.5	Cyclopentanone
5	22.5	6	13	46.2	Methyl i-Propenyl Ketone
5	22.5	5	10	50.0	2-Furaldehyde
5	22.5	8	11	72.7	i-Amyl Chloride
5	22.7	4	18	22.2	2-Methyl-2-Butenoic Acid
5	22.7	4	17	23.5	3-Chloro-3-Methylbutyro-nitirle
5	22.8	5	14	35.7	Hydroxyvaleric Acid Lactone
5	22.9	6	8	75.0	n-Pentylbromide
5	23.0	6	15	40.0	1,1-Methoxyethoxyethane
5	23.1	7	13	53.8	1,2-Dimethylcyclopropane
5	23.2	3	20	15.0	3,4-Pentanediol
5	23.2	4	16	25.0	3-Methyl-1-Butyne
5	23.2	7	10	70.0	2-Bromopentane
5	23.4	4	13	30.8	1-Bromo-2-Methylbutane
5	23.5	3	21	14.3	1,5-Pentanediol
5	23.5	4	14	28.6	Methyl t-Butyl Sulfide
5	23.6	5	15	33.3	Ethoxy Propionitrile
5	23.6	5	15	33.3	Butanediol Formal
5	23.7	4	14	28.6	3,3-Dimethyl-3-Thiabutane
5	23.7	5	10	50.0	Difluoroallyl Acetate
5	23.8	5	14	35.7	3-(1-Thiaethyl) Thiophene
5	23.9	5	19	26.3	Methyl Vinylidine Cyanide
5	24.1	3	14	21.4	3-Bromopyridine
5	24.1	5	9	55.6	3-Methyl-3-Buten-2-one
5	24.2	3	18	16.7	3-Methoxybuteric Acid
5	24.2	5	16	31.3	3-Penten-1-yne
5	24.3	4	15	26.7	2-Chloropyridine
5	24.4	3	11	27.3	1-Bromo-3-Methylbutane
5	24.4	5	11	45.5	1-Bromopentane
5	24.8	6	12	50.0	2,2-Diethyl-1-propanol
5	25.1	4	15	26.7	4-Hydroxy-3-Methyl-2-Butanone
5	25.2	5	13	38.5	2-i-Propoxyethanol
5	25.4	5	12	41.7	1-Chloro-3-Methylbutane
5	25.7	7	10	70.0	1-Pentene
5	25.9	3	12	25.0	Methyl Crotonate
5	25.9	6	11	54.5	2-Methyl-2-Butanol
5	26.2	3	12	25.0	3-Butemyl i-Thiocyanate
5	26.2	6	13	46.2	Ethylcyclopropane
5	26.5	5	10	50.0	i-Amyl Bromide
5	27.0	2	15	13.3	Methyl Hydrogen Succinate
5	27.0	3	11	27.3	Vinyl Acrylate
5	27.1	3	14	21.4	Ethyl Cyanoacetate
5	27.2	5	8	62.5	Methyl Cyclopropyl Ketone
5	27.7	2	17	11.8	1,1-Dichloro-2-Vinyl-cyclopropane
5	27.7	3	13	23.1	Furfuryl Mercaptan
5	27.9	4	12	33.3	1,3-Cyclopentadiene
5	27.9	4	12	33.3	Trimethylacetaldehyde
5	27.9	3	8	37.5	1-Ethoxy-2-Propanol
5	28.4	3	14	21.4	1,1-Bis(Ethylmercapto) Methane
5	28.8	8	10	80.0	2-Methyl-1-Butene
5	29.1	3	10	30.0	Glutaronitrile
5	29.2	4	11	36.4	Methyl Methracrylate
5	29.2	5	11	45.5	2-(2-Methoxyethoxy) Ethanol
5	29.3	4	9	44.4	2-Bromo-2-Methylbutane
5	29.6	4	13	30.8	Pentanoic Acid
5	29.7	2	13	15.4	2-Methyl-1,3-Butanediol
5	29.8	3	9	33.3	3-Chloropyridine
5	30.0	2	11	18.2	2-Bromopyridine
5	30.0	3	10	30.0	2,3-Dithia-4,4-Dimethyl-pentane
5	30.2	4	9	44.4	2,3-Pentanedione
5	30.3	6	10	60.0	2-Methyl-2-Butene
5	30.4	3	9	33.3	2-Ethoxy-1-Propanol
5	30.5	2	13	15.4	2-Methyl-3-butyn-3-ol
5	30.5	4	9	44.4	Pentane
5	30.6	4	10	40.0	2-Pentene
5	30.7	3	9	33.3	3-Bromopentane
5	30.7	4	12	33.3	Methyl i-Butyrate
5	30.8	3	13	23.1	n-Butyl Formate
5	31.0	3	11	27.3	Cyclopentene
5	31.0	4	11	36.4	Methyl i-Butanoate
5	31.2	3	11	27.3	i-Propenyl Trifluoroacetate
5	31.2	5	10	50.0	Chlorocyclopentane
5	31.3	3	13	23.1	2,2-Bis(Methylmercapto) Propane
5	31.6	5	11	45.5	2,2-Dimethyl-1-propanol
5	32.0	2	10	20.0	Ethyl Propanoate
5	32.0	4	11	36.4	Pyridine
5	32.1	3	12	25.0	Valeric Acid
5	32.2	4	12	33.3	Trimethylacetic Acid
5	32.3	2	8	25.0	Cyanovinylacetate
5	32.8	2	11	18.2	2-Methylthiophene

C	Σ_g	N25	N5	R	Compound
5	32.8	3	8	37.5	Furfural
5	33.0	3	9	33.3	Ethyl Propanoate
5	33.0	4	12	33.3	Trimethyl-o-Acetate
5	33.1	6	9	66.7	3-Methyl-1-Butene
5	33.2	4	10	40.0	Methyl t-Butyl Ether
5	33.8	2	11	18.2	2-Chloroallyl Acetate
5	34.0	3	13	23.1	Allyl Vinyl Ether
5	34.1	3	11	27.3	N-Methylmorpholine
5	34.2	2	13	15.4	Cyclopentanol
5	34.5	2	11	18.2	Cyanobutadiene
5	34.6	3	8	37.5	2-Methyl-2-Hydroxybutan-3-one
5	34.7	3	8	37.5	3-Methylthiophene
5	35.0	2	10	20.0	3-Pentanol
5	35.3	3	9	33.3	2,2-Dimethylpropanoic Acid
5	35.7	2	7	28.6	Vinyl Propionate
5	36.3	3	10	30.0	1,3-Dimethoxy-2-Propanol
5	36.6	4	12	33.3	Cyclopentadiene
5	36.8	2	11	18.2	Dimethylamine Propionitrile
5	36.9	3	6	50.0	2,4-Pentanediol
5	37.1	2	11	18.2	2-Methylpyrizine
5	37.2	4	7	57.1	Cyclopentane
5	37.8	2	7	28.6	2-Bromo-3-Pentanone
5	38.0	1	9	11.1	3-Methyl-1-Butyn-3-ol
5	38.1	2	7	28.6	3-Chloropropyl Acetate
5	38.3	1	9	11.1	1-Methoxy-2-Methyl-2-Propanol
5	38.9	1	10	10.0	3-Dimethylamino Propylamine
5	38.9	3	10	30.0	Ethyl i-Propyl Ether
5	39.4	2	12	16.7	2-Pentanone
5	39.4	3	9	33.3	Serine Ethyl Ester
5	41.3	2	9	22.2	2,4-Pentanedione
5	41.3	3	6	50.0	2,2-Dimethylpropane
5	42.1	1	10	10.0	3-Methyl-2-Butanol
5	42.3	3	6	50.0	2-Methoxyethyl Acetate
5	42.7	1	12	8.3	Methyl Acetoacetate
5	42.8	1	10	10.0	Methyl i-Butyl Ether
5	44.7	1	7	14.3	Ethyl Acrylate
5	45.7	2	8	25.0	Methylcyclobutane
5	46.1	2	8	25.0	Levulinic Acid
5	46.3	2	7	28.6	2-Cyanofuran
5	47.1	1	9	11.1	i-Propenyl Acetate
5	48.6	1	7	14.3	3-Methoxy-2-Butanol
5	48.9	1	10	10.0	2-Pentanol
5	49.5	2	6	33.3	Bromocyclopentane
5	50.1	1	9	11.1	i-Propyl Acetate
5	50.2	1	8	12.5	n-Propyl Acetate
5	50.6	1	9	11.1	Glutaraldehyde
5	51.8	1	9	11.1	Methyl Propyl Ketone
5	52.8	1	9	11.1	Methyl 3-Ketobutyrate
5	54.4	1	5	20.0	Acetin
5	56.9	1	5	20.0	Allyl Acetate
5	57.7	1	3	33.3	N-Amylamine
5	58.3	1	4	25.0	Tetramethyldiamino-methane
5	59.5	1	3	33.3	n-Butyl Methyl Ether
5	60.2	1	3	33.3	2-Chloro-1-Cyanoethyl Acetate
5	73.4	1	3	33.3	Alanine Ethyl Ester
5	73.5	1	3	33.3	Propargyl Acetate
6	8.6	14	33	42.4	Thiacycloheptane
6	8.9	12	35	34.3	(2-Hydroxypropyl) n-Propyl Sulfide
6	9.7	9	31	29.0	Hexanal
6	10.1	13	35	37.1	3-Methylthiacyclohexane
6	10.5	11	37	29.7	2,4-Hexadien-1-ol
6	10.5	9	29	31.0	2-Methylcyclopentanethiol
6	11.0	12	42	28.6	2,4-Furandicarboxylic Acid
6	11.1	12	35	34.3	Cyclohexene Sulfide
6	11.3	14	26	53.8	1,6-Hexanediol
6	11.7	12	26	46.2	Cyclohexene Oxide
6	11.9	14	25	56.0	1,2-Cyclohexanediol
6	12.0	12	25	48.0	Hexamethylene Glycol
6	12.0	14	20	70.0	3-Methylpiperidine
6	12.4	9	28	32.1	2,5-Furandicarboxylic Acid
6	12.5	11	21	52.4	3-Methyl-1-Pentanethiol
6	12.6	12	26	46.2	2-Vinyl-4-Methylol-1,3-Dioxolane
6	12.8	10	23	43.5	2-Methyl-3-Pentanethiol
6	12.9	10	30	33.3	7-Thiabicyclo(2,2,1)Heptane
6	12.9	11	18	61.1	Di-n-Propyl Sulfide
6	13.0	10	27	37.0	Cyclohexanethiol
6	13.2	10	22	45.5	3-Thiaheptane
6	13.2	10	22	45.5	Ethyl-n-Butyl Sulfide
6	13.3	7	28	25.0	2-Methyl-3,4-Dihydroxy-tetrahydropyran
6	13.3	10	26	38.5	Methyl-n-Pentyl Sulfide
6	13.3	10	18	55.6	1-Fluorohexane
6	13.6	7	27	25.9	Butynediol Diformate
6	13.8	7	28	25.0	3-Methyl-1,2-Cyclopentanediol
6	13.9	8	25	32.0	2-Hexyne
6	13.9	11	25	44.0	3-Hexanethiol
6	14.0	9	26	34.6	Methyl-n-Amyl Sulfide
6	14.0	9	18	50.0	Pyridine-3-Aldehyde
6	14.1	7	22	31.8	4-Methyl-2-Pentanethiol
6	14.1	7	22	31.8	3-Chloro-3-Methylpentane
6	14.1	8	24	33.3	Adipic Acid
6	14.1	12	20	60.0	2-Hexanethiol
6	14.2	10	25	40.0	2-Methylthiacyclohexane
6	14.2	10	23	43.5	5-Methyl-2-Thiahexane
6	14.3	9	22	40.9	2-Hexenal
6	14.3	10	19	52.6	i-Amyl Formate
6	14.5	9	18	50.0	Chloroacetaldehyde Diethyl Acetal
6	14.6	6	29	20.7	3-Hexyne
6	14.7	7	28	25.0	Kojic Acid
6	14.7	8	21	38.1	Cyclopentyl-1-Thiaethane
6	14.8	10	21	47.6	2-Methoxypyridine
6	15.0	8	27	29.6	Phenylhydrazine
6	15.0	7	21	33.3	Cyclopentylmethanol
6	15.1	9	18	50.0	3,6-Dithiaoctane
6	15.3	9	18	50.0	1-Hexanethiol
6	15.3	9	17	52.9	Methyl i-Pentanoate
6	15.4	9	16	56.3	1-Hexene
6	15.5	8	19	42.1	Vinyl Chloroprene
6	15.5	10	19	52.6	n-Propyl-i-Propyl Sulfide
6	15.5	10	19	52.6	2-Methyl-3-Thiahexane
6	15.6	8	17	47.1	1-Hexanol
6	15.7	7	18	38.9	n-Butyl Chloroacetate
6	15.9	7	23	30.4	(1-Thiaethyl)-Cyclopentane
6	15.9	8	23	34.8	Ethyl Hydroxy-n-Butyrate
6	16.1	8	19	42.1	Hexanenitrile
6	16.5	6	24	25.0	2,4-Hexadienal
6	16.5	6	17	35.3	Ethyl Butanoate
6	16.7	5	22	22.7	2,3-Dimethyl-1,3-Butadiene
6	16.7	8	24	33.3	p-Phenylenediamine
6	16.7	9	17	52.9	2-Ethyl-1-Butene
6	16.8	6	23	26.1	1-Hydrobenzotriazole
6	16.8	7	18	38.9	Butanediol Diformate
6	16.9	7	22	31.8	6-Methyl-3,4-Dithiaheptane
6	16.9	7	17	41.2	i-Butyl Vinyl Ether
6	17.1	4	15	26.7	4-Methyl-3-Penten-2-one
6	17.1	6	21	28.6	2,4-Diamino-2-Methylpentane
6	17.1	7	22	31.8	1-Methylcyclopentanethiol
6	17.1	6	15	40.0	Ethyl-n-Butanoate
6	17.1	8	19	42.1	1,1,1-Trimethoxypropane

C	Σ g	N25	N5	R	Compound
6	17.2	7	17	41.2	4-Methyl-1-Pentyne
6	17.2	7	16	43.8	4-Methyl-3-penten-2-one
6	17.3	5	19	26.3	5-Methyl-2-Furaldehyde
6	17.3	7	22	31.8	4-Methyl-3-Thiahexane
6	17.3	7	15	46.7	n-Butyl Vinyl Ether
6	17.4	6	20	30.0	3-Methyl-3-Pentanethiol
6	17.5	6	20	30.0	2-(Methylallyloxy) Ethanol
6	17.5	8	22	36.4	Ethyl-i-Butyl Sulfide
6	17.5	8	21	38.1	5-Methyl-3-Thiahexane
6	17.7	6	21	28.6	Dipropargylamine
6	17.7	6	17	35.3	Butanediol Diformate
6	17.7	7	18	38.9	1,2-Bis(Ethylmercapto) Ethane
6	17.8	5	22	22.7	2-Ethyl-4-Methylol-1,3-Dioxolane
6	17.9	6	15	40.0	Ethyl Ethoxyacetate
6	17.9	7	15	46.7	Di-i-Propyl Sulfide
6	18.0	8	17	47.1	2-Methylpiperazine
6	18.0	7	13	53.8	Hexane
6	18.1	6	20	30.0	Methoxyethoxypropane
6	18.1	8	15	53.3	3-Methyl-1-Pentene
6	18.2	7	12	58.3	2,2-Dimethylbutane
6	18.4	5	16	31.3	3-Hexen-1-ol
6	18.4	6	16	37.5	2-Ethylbutanoic Acid
6	18.4	7	17	41.2	Vinyl i-Butyl Ether
6	18.4	7	15	46.7	3-Methyl-1-Pentanol
6	18.5	4	23	17.4	1,3,3-Trimethoxy-1-Propene
6	18.5	3	15	20.0	3-Hexene
6	18.5	7	18	38.9	1-Hexyne
6	18.5	9	17	52.9	1-Methyl-1-Ethyl-cyclopropane
6	18.6	6	14	42.9	Chlorocyclohexane
6	18.7	4	16	25.0	2,3-Dimethylthiophene
6	18.7	7	19	36.8	5-Methyl-3,4-Dithiaheptane
6	18.8	5	19	26.3	4-Thia-1,6-Heptadiene
6	18.9	7	16	43.8	1-Chlorohexane
6	18.9	9	19	47.4	3-Hexen-1-ol
6	19.0	4	23	17.4	3-Cyclohexen-1-ol
6	19.1	5	19	26.3	2,5-Dimethylol-1,4-Dioxane
6	19.1	7	16	43.8	2-Methanol Tetraahydropyran
6	19.2	7	16	43.8	2-Methyl-1-Pentanethiol
6	19.2	7	15	46.7	1,5-Hexadiyne
6	19.3	8	17	47.1	3-Hexanol
6	19.4	8	15	53.3	Methyl-n-Pentanoate
6	19.6	8	15	53.3	2-Hexene
6	19.6	7	12	58.3	3,3-Diethyl-2-Butanol
6	19.7	6	16	37.5	4-Methyl-2-Ethyl-1,3-Dioxolane
6	19.7	8	14	57.1	2-Methyl-1-Pentene
6	19.8	6	18	33.3	Dimethyl Succinate
6	19.9	7	16	43.8	2,2-Dimethyl-1-Butanol
6	20.0	3	19	15.8	2,5-Dimethylthiophene
6	20.0	2	10	20.0	2-Methyl-3-Pentanol
6	20.0	6	17	35.3	2-Chlorocyclohexanone
6	20.1	5	21	23.8	1-Methyl-2-Pyridone
6	20.2	5	21	23.8	2-Methyl-1,3-Pentadiene
6	20.3	5	20	25.0	m-Dichlorobenzene
6	20.3	6	22	27.3	2-Ethyl-2-(Hydroxymethyl)-1,3-Propanediol
6	20.3	5	16	31.3	2,5-Dimethylthia-cyclopentane
6	20.4	6	15	40.0	2-Methyl-2-Pentenal
6	20.4	7	14	50.0	Cyclohexane
6	20.5	5	14	35.7	2,4-Dimethyl-3-Thiapentane
6	20.6	6	15	40.0	2-Methylpentanal
6	20.7	3	24	12.5	1-Fluorocyclohexene
6	20.7	4	19	21.1	1-i-Propoxy-2-Propanol
6	20.7	4	18	22.2	2-Hydroxycyclohexanone
6	20.7	6	15	40.0	Triethanolamine
6	20.8	4	15	26.7	Amyl Formate
6	20.8	7	17	41.2	Cyclohexanone
6	20.8	7	16	43.8	4,5-Dimethyl Dioxane
6	20.8	6	10	60.0	3-Hexanone
6	20.9	3	19	15.8	Benzenethiol
6	20.9	6	16	37.5	Vinyl n-Butyl Ether
6	20.9	6	14	42.9	1-Bromohexane
6	21.0	4	20	20.0	2-Hexen-4-yne
6	21.0	4	19	21.1	1,4-Bis(Methylmercapto) Butane
6	21.1	4	17	23.5	Allyl Acrylate
6	21.2	6	15	40.0	2-(2-Ethoxyethoxy) Ethanol
6	21.3	5	13	38.5	Bis(2-Hydroxypropyl) Ether
6	21.4	4	20	20.0	Vinylthiophene
6	21.4	6	14	42.9	Caprolactone
6	21.6	4	13	30.8	3,3-Bis(Hydroxymethyl) 2-Butanone
6	21.6	5	16	31.3	i-Propyl 3-Chloropropionate
6	21.7	6	13	46.2	1-Bromo-3-Methylpentane
6	21.8	6	14	42.9	Allylethyl Carbonate
6	21.9	5	15	33.3	2-n-Butoxyethanol
6	21.9	7	17	41.2	4-Methylpentanenitrile
6	22.0	7	11	63.6	Dimethyl Sulfolane
6	22.2	4	17	23.5	o-Fluorophenol
6	22.2	4	15	26.7	Hydroxyethyl Methacrylate
6	22.3	4	13	30.8	Ethyl Methacrylate
6	22.4	3	22	13.6	3,3-Prim Iminobispropyl
6	22.4	6	14	42.9	3,3-Dimethyl-2-Thiapentane
6	22.5	5	20	25.0	Diallylamine
6	22.6	5	17	29.4	2,6-Dimethylol-1,4-Dioxane
6	22.6	5	11	45.5	2-Methyl-3-Pentanone
6	22.6	6	11	54.5	4-Methyl-2-Pentanone
6	22.9	4	13	30.8	Tetramethyl Ethylene Oxide
6	23.0	5	18	27.8	3-Methylpyridine
6	23.0	5	14	35.7	1,5-Hexadiene
6	23.0	6	16	37.5	1,3,5-Hexatriene
6	23.1	5	14	35.7	1,2-Dimethylene Cyclobutane
6	23.1	8	14	57.1	2-Ethyl-1-Butanol
6	23.2	6	14	42.9	Dipropargyl Ether
6	23.3	7	16	43.8	2-Ethyl-n-Butanol
6	23.4	5	17	29.4	Cyclohexene
6	23.6	2	10	20.0	p-Fluoroanaline
6	23.6	4	15	26.7	2,4-Dimethylthiophene
6	23.6	4	15	26.7	Dipropylene Glycol
6	23.7	3	17	17.6	gamma-Picoline
6	23.7	6	10	60.0	3-Methylpentane
6	23.8	6	16	37.5	Hexanoic Acic
6	24.1	4	15	26.7	2-Methyl-2-penten-1-al
6	24.1	4	14	28.6	4-Hydroxy-4-Methyl-2-pentanone
6	24.2	5	14	35.7	Naphthodioxane
6	24.3	5	16	31.3	2,5-Dimethylpiperazine
6	24.4	4	13	30.8	Di-1-Propylamine
6	24.4	5	14	35.7	3,4-Dimethyl-2-Thiapentane
6	24.5	3	19	15.8	i-Propenylcyclopropane
6	24.5	4	19	21.1	2-Ethyl Thiolane
6	24.6	3	19	15.8	2-Methylpyridine
6	24.6	5	19	26.3	Fluorocyclohexane
6	24.6	5	14	35.7	1-Chloro-3-Nitrobenzene
6	24.7	3	15	20.0	3,7,9-Trioxabicyclo (3.3.1) Nonane
6	24.7	4	19	21.1	2-Hexen-1-ol
6	24.7	6	16	37.5	Cyclohexanol
6	24.7	5	12	41.7	Methylcyclopentane
6	25.1	4	18	22.2	2-Amino-6-Methylpyridine
6	25.1	4	16	25.0	2-Hydroxy-3-Methyl-2-Cyclopenten-1-one
6	25.1	5	12	41.7	6-Hydroxyhexanoic Acid Lactone
6	25.2	6	13	46.2	2-Methyl-1-Pentanol

C	Σ_g	N25	N5	R	Compound
6	25.3	3	18	16.7	m-Chloroanaline
6	25.3	3	13	23.1	1,4-Cyclohexadiene
6	25.5	2	21	9.5	Hydroquinone
6	25.5	3	15	20.0	2-Methylpentanoic Acid
6	25.5	3	11	27.3	Hexamethyl Disiloxane
6	25.5	5	13	38.5	Ethyl-i-Butyrate
6	25.6	3	12	25.0	Bromobenzene
6	25.7	3	14	21.4	o-Dichlorobenzene
6	25.7	6	10	60.0	Bis(2-Methoxyethyl) Ether
6	25.9	3	11	27.3	2-Methylvaleraldehyde
6	25.9	4	10	40.0	Allyl Propionate
6	26.0	4	14	28.6	2-Vinylpyrrolidone
6	26.1	4	14	28.6	2-Ethyl-1-Butanol
6	26.2	4	15	26.7	2-Methyl-2-Pentene
6	26.2	5	13	38.5	1,5-Hexadien-3-yne
6	26.5	5	15	33.3	Acetone Azide
6	26.6	4	15	26.7	1,3-Cyclohexadiene
6	26.7	3	14	21.4	4-Methyl-1-Pentanethiol
6	26.7	4	15	26.7	2,2-Dimethyl-3-Thiapentane
6	27.0	4	14	28.6	2,3-Dimethyl-2-Butene
6	27.0	4	10	40.0	2-Methoxyethyl Acrylate
6	27.1	2	14	14.3	3,3-Dimethyl-1-Butene
6	27.1	4	14	28.6	1,2-Bis(Vinyloxy) Ethane
6	27.3	2	11	18.2	2,3-Dichloroanaline
6	27.3	4	14	28.6	Ethyl-t-Butyl Sulfide
6	27.3	4	13	30.8	5-Hydroxyhex-1-ene
6	27.3	5	9	55.6	Quinone
6	27.4	4	12	33.3	1,2-Hexanediol
6	27.7	2	14	14.3	Acetylbuterolactone
6	27.7	5	8	62.5	1,2-Diethoxyethane
6	27.7	5	8	62.5	1,2-Diethoxyethane
6	27.8	3	14	21.4	4,4-Dimethyldioxane
6	27.8	4	14	28.6	5-Methyl-1,3-Cyclopentadiene
6	28.0	2	19	10.5	o-Nitrophenol
6	28.0	3	17	17.6	3,3-Dimethyl-4-Hydroxy-2-Butanone
6	28.0	3	12	25.0	2,6-Dichlorophenol
6	28.1	2	13	15.4	2,4-Dimethylpyrrole
6	28.1	4	15	26.7	Triethylamine
6	28.3	2	15	13.3	2-Amino-3-Methylpyridine
6	28.4	2	13	15.4	3-Methyl-1-Pentyn-3-ol
6	28.4	3	13	23.1	3-Bromohexane
6	28.6	2	11	18.2	3,4-Dichloroanaline
6	28.6	3	13	23.1	Nitrobenzene
6	28.6	4	14	28.6	2,4-Hexadiyne
6	28.6	4	10	40.0	2,5-Dimethylpyrazine
6	28.8	9	16	56.3	n-Propyl Propionate
6	29.0	3	12	25.0	2-Ethynyl-2-Butanol
6	29.3	3	11	27.3	4,5-Dithiaoctane
6	29.3	3	10	30.0	Ethylcyclobutane
6	29.5	4	14	28.6	Butadiene Acetylene
6	29.6	3	16	18.8	Allyl Ether
6	29.7	2	12	16.7	1,1-Dimethylbutanol
6	29.7	3	9	33.3	1-Acetoxy-2-Butanone
6	29.9	4	12	33.3	i-Propyl Propionate
6	30.0	3	12	25.0	2-Methyl-2,4-Pentanediol
6	30.0	3	12	25.0	2-t-Butoxyethanol
6	30.0	3	11	27.3	Adiponitrile
6	30.0	5	9	55.6	Diglyme
6	30.1	2	12	16.7	2,3-Dimethylpyrazine
6	30.4	3	17	17.6	Ethyl Acetoacetate
6	30.5	3	12	25.0	Furfuryl Methyl Ether
6	30.5	3	11	27.3	2-Bromohexane
6	30.6	3	8	37.5	2,3-Dimethylbutane
6	30.7	2	14	14.3	Catechol
6	30.8	3	13	23.1	Methylene Cyclopentane
6	30.8	4	14	28.6	1,1,2-Trimethylcyclopropane
6	31.0	3	16	18.8	2,2-Dimethyl-4-Methylol-1,3-Dioxolane
6	31.1	3	10	30.0	o-Fluorochlorobenzene
6	31.3	5	8	62.5	Methyl t-Butyl Ketone
6	31.4	3	11	27.3	2-Methylthio-5-Methylfuran
6	31.6	2	9	22.2	2,5-Dichlorophenol
6	31.8	4	10	40.0	Methyl Furoate
6	32.0	4	10	40.0	2-Methylpentane
6	32.1	3	12	25.0	1.1-Diethoxyethane
6	32.3	3	13	23.1	Phenol
6	32.4	5	18	27.8	2,6-Dimethylpyrazine
6	32.5	3	11	27.3	Ethyl t-Butyl Ether
6	32.6	2	11	18.2	3-Methyl-1-Pentyn-3-ol
6	32.6	3	9	33.3	Vinyl Methacrylate
6	32.6	5	8	62.5	t-Butyl Acetate
6	33.1	3	9	33.3	2-Ethylbuteraldehyde
6	33.4	2	13	15.4	2-Methyl-3-Hydroxypyrrone
6	33.8	2	11	18.2	2,5-Hexanediol
6	33.8	2	10	20.0	m-Chlorophenol
6	33.8	3	8	37.5	3-Ethylthiophene
6	34.1	3	10	30.0	3,3-Dimethyl-1-Butyne
6	34.1	3	7	42.9	Vinyl Butyrate
6	34.2	3	9	33.3	p-Dichlorobenzene
6	34.2	4	11	36.4	3-Methyl-2-Pentanone
6	34.3	2	11	18.2	Methyl Propyl Keytone
6	34.3	3	9	33.3	3,3-Dimethyl-1-butyne
6	34.4	2	12	16.7	Analine
6	34.5	4	7	57.1	Bis(1-Methyl-2-Hydroxypropyl) Ether
6	34.7	2	10	20.0	n-Butyl Acetate
6	34.9	2	12	16.7	3-Methylcyclopentene
6	35.1	2	11	18.2	4-Methylcyclopentane
6	35.2	2	10	20.0	Butadienyl-4-Acetate
6	35.3	3	8	37.5	o-Chlorophenol
6	35.6	2	14	14.3	2,4-Dimethyl-2-Methylol-1,3-Dioxolane
6	35.6	2	9	22.2	2,3-Dimethyl-2-Butanol
6	35.6	2	7	28.6	2-Ethylthiophene
6	35.9	2	9	22.2	Methyl i-Butyl Ketone
6	36.0	2	10	20.0	Di-2-Propylamine
6	36.1	2	11	18.2	1-Methylcyclopentene
6	36.2	2	10	20.0	2-Methyl-2-Pentanol
6	36.5	2	12	16.7	4-Methyl-2-Pentanol
6	36.7	3	7	42.9	2-i-Propoxy-1-Propanol
6	36.8	2	9	22.2	1,1-Bis(Ethylmercapto) Ethane
6	36.8	2	7	28.6	2,2,4-Trimethyl-1,3-Dioxolane
6	37.1	2	10	20.0	Triethylene Glycol
6	37.2	2	8	25.0	p-Chlorophenol
6	37.2	4	12	33.3	2,4-Dichlorophenol
6	37.7	2	8	25.0	2,5-Dimethyl-3,4-Dithiahexane
6	38.0	2	8	25.0	2-Diethylaminoethanol Hydrochloride
6	38.1	2	10	20.0	4-Methyl-2-Pentanone
6	38.1	4	8	50.0	2-(2-Hydroxypropoxy)-1-Propanol
6	38.3	1	12	8.3	4-Chlorocyclohexanol
6	38.3	2	8	25.0	Pyrocatechol
6	38.3	6	16	37.5	2-Methyl-2-Pentanethiol
6	38.5	6	11	54.5	4-Methyl-2-Pentanone
6	38.7	2	11	18.2	Cyclohexylamine
6	38.9	2	14	14.3	Cyclohex-2-en-1-one
6	38.9	2	10	20.0	Methallyl Acetate
6	39.1	2	8	25.0	2-Hexanone
6	39.1	3	11	27.3	Benzofurazan
6	39.2	3	7	42.9	Chlorobenzene
6	39.4	1	8	12.5	Di-i-Propyl Ether
6	39.9	2	8	25.0	N-Ethyl-N-Butyl Amine
6	39.9	3	8	37.5	t-Butyl Acetate
6	40.3	3	5	60.0	Propanoic Anhydride

C	Σ_g	N25	N5	R	Compound
6	40.6	2	8	25.0	Bromocyclohexane
6	40.8	1	9	11.1	i-Butyl Acetate
6	41.0	2	9	22.2	Diacetone Alcohol
6	41.7	1	11	9.1	Ethyl 3-Ketobutyrate
6	41.7	3	7	42.9	Paraldehyde
6	41.8	1	9	11.1	2-Hexanol
6	41.9	1	9	11.1	Di-n-Propyl Ether
6	41.9	3	8	37.5	4-Methyl-1-Pentyn-1-ol
6	42.3	1	8	12.5	p-Fluorophenol
6	42.3	2	8	25.0	N-Methylpiperidine
6	43.0	2	8	25.0	2,4,6-Trimethyl-1,3,5-Trioxacyclohexane
6	43.5	2	5	40.0	Furyl Methyl Ketone
6	43.6	2	8	25.0	Diacetoneamine
6	44.4	2	8	25.0	Methyl 2-Methyl-3-Ketobutyrate
6	44.6	1	8	12.5	Resorcinol
6	44.6	1	8	12.5	2-Butylacetate
6	44.6	3	5	60.0	Hexamethylene Tetramine
6	45.2	1	8	12.5	Benzene
6	46.3	2	7	28.6	2,2-Bis(Dioxolanyl-1,3)
6	46.4	1	7	14.3	2-(2-Vinyloxyethoxy) Ethanol
6	46.8	1	6	16.7	Threo-3-Chloro-2-Acetoxybutane
6	46.9	1	8	12.5	Hexamethylene Diamine
6	47.1	1	7	14.3	5-Hexen-2-one
6	47.8	1	7	14.3	4-Methyl-2,3-Pentanedione
6	48.1	2	6	33.3	Ethyl Hydroxy-i-Butyrate
6	49.9	1	6	16.7	2,5-Hexanedione
6	51.0	1	8	12.5	2,3,3,2-Thiophenothiophene
6	51.6	1	6	16.7	Diethyl Oxylate
6	51.7	1	7	14.3	Di(Acetyl Cyanide)
6	51.9	2	3	66.7	Dimethyl Fumarate
6	52.4	2	6	33.3	2,5-Hexanedione
6	52.4	2	5	40.0	2-Acetylfuran
6	52.6	1	5	20.0	Methoxyacetic Anhydride
6	53.6	1	6	16.7	Fluorobenzene
6	58.4	2	3	66.7	Hydroxyadipaldehyde
6	59.2	2	3	66.7	Methyl Thiofuroate
6	59.9	2	5	40.0	Methyl Furan-2-Carboxylate
6	60.7	1	5	20.0	2,3-Dimethyl-2,3-Butanediol
6	63.2	1	4	25.0	1,2-Ethane Diacetate
6	63.2	1	3	33.3	N-Hexylamine
7	8.4	11	42	26.2	2-Thiabicyclo (2.2.2) Octane
7	8.7	13	41	31.7	2-Thiabicyclo (3.3.3.0) Octane
7	9.2	13	37	35.1	Methyl-4-Hexenoate
7	9.3	12	28	42.9	n-Heptanal
7	9.5	12	29	41.4	2-Heptenal
7	9.5	16	27	59.3	2-Methyl-3-Thiaheptane
7	9.8	11	27	40.7	Heptaldehyde
7	9.9	13	34	38.2	2,4-Heptadienal
7	10.0	8	49	16.3	1,2-Propanediol Diacetate
7	10.0	11	38	28.9	2-Hydroxycyclohexane-carboxylic Acid
7	10.0	13	29	44.8	3-Heptyne
7	10.1	13	25	52.0	1-Heptanethiol
7	10.2	10	39	25.6	2-Thiabicyclo (3.3.0) Octane
7	10.3	12	24	50.0	n-Heptyl Alcohol
7	10.5	11	35	31.4	8-Thiabicyclo (3.2.1) Octane
7	10.6	12	41	29.3	3-Thiabicyclo (3.3.0) Octane
7	10.6	9	29	31.0	5-Methyl-2-Hexyne
7	10.7	11	22	50.0	Cycloheptane
7	10.7	14	25	56.0	i-Propyl n-Butyl Sulfide
7	10.8	13	31	41.9	2,3-Dimethylpiperidine
7	10.9	10	30	33.3	3,7-Dithianonane
7	11.2	10	31	32.3	Pimelic Acid
7	11.2	12	29	41.4	2-Thiooctane
7	11.2	11	25	44.0	n-Propyl i-Butyl Sulfide
7	11.3	8	41	19.5	2,6-Dimethoxypyridine
7	11.3	11	31	35.5	3-Methoxy-1,3,4-Hexatriene
7	11.4	12	29	41.4	Methyl n-Hexyl Sulfide
7	11.7	10	24	41.7	Cycloheptene
7	11.7	13	25	52.0	n-Propyl-n-Butyl Sulfide
7	11.7	10	19	52.6	2-Methyl-2-Propyl-1,3-Propanediol
7	11.9	8	37	21.6	Methyl Sorbate
7	12.1	9	29	31.0	Cyclohexane Carboxylic Acid
7	12.1	14	27	51.9	Methyl Hex-2-Enoate
7	12.2	9	35	25.7	Methyl 5-Hexenoate
7	12.3	9	30	30.0	3-Hepten-1-ol
7	12.4	11	27	40.7	1-Heptyne
7	12.5	9	26	34.6	2-Heptyne
7	12.7	9	25	36.0	2-Ethoxypyridine
7	12.8	9	27	33.3	Methyl i-Hexanoate
7	13.0	9	30	30.0	Methyl Nicotinate
7	13.0	12	27	44.4	2-Methylcyclohexanol
7	13.2	9	25	36.0	2,5-Dimethyl-3-Thiahexane
7	13.4	12	21	57.1	1-Chloroheptane
7	13.6	10	26	38.5	2,2-Dimethyl-3,4-Pentadienol
7	13.7	9	29	31.0	Methyl-3-Hexenoate
7	13.8	9	24	37.5	Ethyl i-Valerate
7	13.9	11	24	45.8	Ethyl Ethoxypropionate
7	14.0	8	26	30.8	1-sec-Butoxy-2-Propanol
7	14.0	9	17	52.9	1-Fluoroheptane
7	14.1	10	24	41.7	Toluquinone
7	14.1	12	26	46.2	3-Methyl Cyclohexanol
7	14.1	10	20	50.0	Ethylcyclopentane
7	14.3	7	18	38.9	5-Methylhexanol
7	14.4	8	27	29.6	2-Methyl-2-Hexanethiol
7	14.4	9	26	34.6	3-Cyclohexene-1-Carboxaldehyde
7	14.5	10	19	52.6	2-Methyl-1,5-Hexadiene
7	14.6	6	34	17.6	p-Methoxyphenol
7	14.7	7	19	36.8	3-Methyl-1-Hexanol
7	14.7	9	18	50.0	3-Methyl-1-Hexanol
7	14.9	7	26	26.9	o-Cresol
7	14.9	9	22	40.9	n-Heptanenitrile
7	14.9	8	19	42.1	2-Heptene
7	15.0	7	19	36.8	3-Methyl-2-Ethyl-1-Butene
7	15.2	10	23	43.5	Dimethyl (Vinylethinyl) Carbinol
7	15.3	10	16	62.5	1-Heptene
7	15.4	8	25	32.0	2,2-Dimethyl-3,4-Pentadienal
7	15.6	6	31	19.4	7,7-Dichlorobicyclo (4,1,0) Heptane
7	15.6	8	24	33.3	5-Methyl-1-Hexyne
7	15.6	8	18	44.4	3-Methyl-1-Hexene
7	15.7	8	21	38.1	Heptanoic Acid
7	15.7	9	18	50.0	1,3-Dimethylcyclopentane
7	16.0	7	21	33.3	Ethyl n-Valerate
7	16.0	9	22	40.9	2,4-Dimethyl-3-Thiahexane
7	16.0	9	22	40.9	i-Propyl s-Butyl Sulfide
7	16.1	8	17	47.1	2-Chloroheptane
7	16.1	9	16	56.3	1,6-Heptadiene
7	16.4	5	25	20.0	1,3-Bis(Ethylmercapto) Propane
7	16.5	5	21	23.8	Benzyl Alcohol
7	16.6	8	17	47.1	1,1-Dimethylcyclopentane
7	16.7	5	19	26.3	Methallyl Propyl Ether
7	16.7	7	18	38.9	3-Ethyl-2-Pentene
7	16.7	8	16	50.0	Butyl Lactate
7	16.7	9	17	52.9	3,4-Dimethyl-1-Pentanol
7	16.9	6	18	33.3	Acetone Methyl Propyl Acetal
7	16.9	8	18	44.4	Norbornylane
7	17.2	8	20	40.0	Methylcyclohexane
7	17.2	8	20	40.0	Allyl Acetothioacetate

C	Σ_g	N25	N5	R	Compound
7	17.2	8	14	57.1	2,3-Dimethylpentane
7	17.3	6	18	33.3	5-Methyl-2-Hexene
7	17.4	7	17	41.2	2,2-Diethyl-1,3-Propanediol
7	17.4	8	17	47.1	5-Methyl-1-Hexene
7	17.4	8	16	50.0	Cycloheptanone
7	17.4	9	16	56.3	1,1-Diethoxypropane
7	17.5	6	25	24.0	3-Methylcyclohexanol
7	17.5	8	22	36.4	Furfuryl Acetate
7	17.6	6	24	25.0	4-Methyl-2-Hexyne
7	17.6	7	18	38.9	Dimethyl Glutarate
7	17.6	8	18	44.4	Methyl Caproate
7	17.7	7	26	26.9	m-Methoxyphenol
7	17.9	6	16	37.5	m-Nitrobenzaldehyde
7	17.9	9	16	56.3	n-Hexyl Formate
7	18.0	6	23	26.1	3-Fluorosalicylic Acid
7	18.0	9	17	52.9	1,2-Dimethylcyclopentane
7	18.1	6	20	30.0	Hydroxypropyl Methacrylate
7	18.1	9	17	52.9	3-Methyl-1-Cyclohexene
7	18.2	5	25	20.0	Chlorophenyl i-Cyanate
7	18.2	7	20	35.0	1-Methylcyclohexene
7	18.3	5	21	23.8	2,6-Dimethylpiperidine
7	18.5	7	21	33.3	2,4-Dimethyl-1,3-Pentadiene
7	18.6	6	20	30.0	3-Ethylpyridine
7	18.6	6	18	33.3	3-Methylcyclohexanone
7	18.6	6	16	37.5	n-Propyl n-Butyrate
7	18.7	5	17	29.4	o-Nitrotoluene
7	18.7	5	17	29.4	p-Nitrobenzaldehyde
7	18.7	6	17	35.3	Cyclohexyl Formate
7	18.8	4	24	16.7	Cyclohexanecarboxaldehyde
7	18.8	6	16	37.5	2-Vinylpyridine
7	18.8	6	14	42.9	4-Methyl-1-Hexene
7	19.0	5	19	26.3	1-i-Butoxy-2-Butanol
7	19.0	6	18	33.3	3-Methyl-3-Hexene
7	19.1	7	23	30.4	3-Methyl-1-Cyclohexene
7	19.2	6	21	28.6	5-Hydroxymethyl-4,5-Dimethyl-1,3-Dixoane
7	19.3	5	22	22.7	Phenylisocyanate
7	19.3	5	16	31.3	Benzoic Acid
7	19.3	6	17	35.3	3-Acetylpyridine
7	19.3	6	16	37.5	3-Methylhexanal
7	19.3	6	16	37.5	m-Chlorobenzoic Acid
7	19.3	8	14	57.1	3-Methyl-3-Hexanol
7	19.4	5	18	27.8	3-Cyclohexene-1-Carboxylic Acid
7	19.4	6	20	30.0	t-Butyl Trioxane
7	19.5	5	17	29.4	4-Chloro-o-Cresol
7	19.5	5	15	33.3	1,1,2,2-Tetramethylcyclo-propane
7	19.5	7	18	38.9	3-Heptene
7	19.6	7	17	41.2	p-Methylcyclohexanol
7	19.7	5	22	22.7	m-Cresol
7	19.8	6	16	37.5	4,4-Dimethyl-2-Pentene
7	19.8	7	17	41.2	Methyl Hexanoate
7	19.9	4	13	30.8	m-Hydroxybenzoic Acid
7	19.9	5	13	38.5	m-Chlorobenzaldehyde
7	19.9	7	18	38.9	3-Methyl-2-Hexene
7	20.0	4	20	20.0	2,3,4-Trimethylthiophene
7	20.0	6	17	35.3	2,3-Dimethyl-1-Pentene
7	20.0	7	17	41.2	3-Heptanol
7	20.1	6	21	28.6	1,5-Bis(Methylmercapto) Pentane
7	20.2	3	16	18.8	Methyl Analine
7	20.2	6	17	35.3	4-Methylcyclohexanone
7	20.5	7	14	50.0	2,3-Dimethyl-3-Pentanol
7	20.6	5	16	31.3	1,2-Heptanediol
7	20.7	5	19	26.3	Benzyl Amine
7	20.7	6	21	28.6	4-Hydroxymethyl-4,5-Dimethyl-1,3-Dioxane
7	20.8	4	15	26.7	p-Chlorobenzaldehyde
7	20.8	5	16	31.3	Benzaldehyde
7	20.8	8	12	66.7	3-Methylhexane
7	20.9	3	23	13.0	2,3-Dimethylpyridine
7	20.9	6	18	33.3	4-Ethylpyridine
7	21.0	4	18	22.2	5-Chlorosalicylaldehyde
7	21.0	6	19	31.6	6-Thiabicyclo (3.2.1) Octane
7	21.0	5	14	35.7	1-Heptene-4-ol
7	21.1	4	20	20.0	2-Methylcyclohexanethiol
7	21.3	5	16	31.3	2-Methyl-3-Hexanol
7	21.4	5	17	29.4	Cyclohexanemethanol
7	21.4	6	13	46.2	1-n-Butoxy-2-Propanol
7	21.5	6	18	33.3	3-Vinylpyridine
7	21.6	3	21	14.3	Cylcoheptanol
7	21.6	4	16	25.0	p-Chlorobenzoic Acid
7	21.6	4	14	28.6	o-Chlorobenzaldehyde
7	21.8	4	24	16.7	3,4-Dimethylpyridine
7	21.8	6	18	33.3	4-Methylcyclohexene
7	21.8	6	18	33.3	4-Vinylpyridine
7	21.8	5	13	38.5	3-Ethyl-3-Pentanol
7	21.9	7	13	53.8	n-Heptane
7	22.0	4	24	16.7	2,5-Dimethylpyridine
7	22.1	5	15	33.3	n-Propyl n-Butyl Ether
7	22.2	5	16	31.3	Ethoxyacetaldehyde Methyl Vinyl Acetal
7	22.3	5	19	26.3	Ethyl Methyl Dioxane
7	22.4	5	16	31.3	3-Ethyl-1-Pentene
7	22.4	5	15	33.3	3,3-Dimethyl-1-Pentene
7	22.5	4	23	17.4	3,5-Dimethylpyridine
7	22.7	3	16	18.8	1,5-Heptadien-3-yne
7	22.7	4	13	30.8	i-Propyl Butyrate
7	22.8	4	15	26.7	(1-Thiaethyl) Benzene
7	22.8	6	16	37.5	2-Methyl-2-Hexene
7	22.9	3	15	20.0	2,6-Dimethyl-4-Pyrone
7	23.0	4	15	26.7	2,3,3-Trimethyl-1-Butene
7	23.0	5	16	31.3	Ethyl 2-Methylbutyrate
7	23.1	4	16	25.0	1-Cyclohexene-1-Carboxylic Acid
7	23.2	4	17	23.5	Allyl Methacrylate
7	23.5	4	13	30.8	i-Propyl Crotonate
7	23.6	4	14	28.6	m-Aminobenzoic Acid
7	23.6	5	15	33.3	Diethyl Malonate
7	23.6	5	11	45.5	m-Hydroxybenzaldehyde
7	23.7	4	14	28.6	4,4,5-Trimethyl-5-Hydroxy-1,3-Dioxane
7	23.8	4	10	40.0	Allyl n-Butanoate
7	23.8	6	10	60.0	2,2,3-Trimethylbutane
7	23.9	6	16	37.5	2,4-Dimethyl-3-Pentanol
7	24.0	3	12	25.0	2-Methyladiponitrile
7	24.0	4	15	26.7	Di-i-Propylcarbinol
7	24.0	4	9	44.4	4-Chloro-2-Fluoroanisole
7	24.1	3	19	15.8	Methionine Ethyl Ester
7	24.1	3	17	17.6	p-Nitrotoluene
7	24.2	1	24	4.2	Orcinol
7	24.2	4	14	28.6	o-Chlorobenzoic Acid
7	24.3	4	17	23.5	2-Methyl-5-Ethylpyrazine
7	24.3	4	13	30.8	o-Phenylene Cyclic Carbonate
7	24.4	2	19	10.5	Ethyl Levulinate
7	24.4	3	7	42.9	p-Fluoroanisole
7	24.5	3	13	23.1	m-Toluidine Hydrochloride
7	24.5	4	15	26.7	Methyl Phenyl Ether
7	24.5	4	15	26.7	Benzoyl Fluoride
7	24.7	5	14	35.7	2,4-Dimethyl-1-Pentene
7	24.9	3	17	17.6	3-Methylprocatechol
7	25.0	2	10	20.0	Di-n-Propoxymethane
7	25.1	5	12	41.7	2,6-Dichlorotoluene
7	25.2	2	19	10.5	o-Toluidine
7	25.3	5	10	50.0	2,4-Dimethylpentane
7	25.5	6	14	42.9	Ethenylcyclopentane
7	25.6	2	16	12.5	i-Propyl t-Butyl Sulfide
7	25.7	4	12	33.3	3-Ethyl-1-Pentyn-3-ol

C	Σ_g	N25	N5	R	Compound
7	25.8	6	8	75.0	2,2-Dimethylpentane
7	26.0	3	15	20.0	2,2-Dimethyl-1-Pentanol
7	26.0	2	9	22.2	o-Fluoroanisole
7	26.0	5	19	26.3	p-Cresol
7	26.0	2	3	66.7	Benzaldehyde Oxime
7	26.1	4	13	30.8	2,4-Dichlorotoluene
7	26.1	4	10	40.0	Benzotrifluoride
7	26.6	3	14	21.4	1,2-Bis(Ethylmercapto) Propane
7	26.7	4	14	28.6	Triethylene Glycol Methyl Ether
7	26.7	5	10	50.0	1,1,1-Triethoxy Methane
7	26.8	3	17	17.6	2,6-dimethylpyridine
7	26.9	4	11	36.4	Neopentyl Acetate
7	27.0	2	12	16.7	Salicylaldehyde
7	27.0	3	12	25.0	4-Chloro-m-Cresol
7	27.2	2	15	13.3	Pyruvaldehyde Diethyl Acetate
7	27.3	2	21	9.5	2,4-Dimethylpyridine
7	27.3	2	18	11.1	Methyl 2-Methylvalerate
7	27.4	3	15	20.0	Diethylaminopropyl Alcohol
7	27.5	2	12	16.7	Methyl n-Hexanoate
7	27.6	3	10	30.0	Phenyl i-Thiocyanate
7	27.8	2	10	20.0	2,4-Dimethyl Pentanal
7	27.9	2	9	22.2	2,4-Toluenediamine
7	28.1	3	11	27.3	o-Toluidine Hydrochloride
7	28.1	4	11	36.4	3-Heptanone
7	28.2	3	13	23.1	6-Chloro-o-Cresol
7	28.3	3	17	17.6	n-Propyl Acetoacetate
7	28.4	4	12	33.3	n-Amyl Acetate
7	28.7	5	9	55.6	2-Methylhexane
7	28.8	5	16	31.3	1-Butoxy-2-Methoxyethane
7	28.8	4	10	40.0	Benzoyl Chloride
7	29.0	4	12	33.3	3,4-Dichlorotoluene
7	29.3	3	9	33.3	1,1-Dipropoxyethane
7	29.4	3	16	18.8	Benzothiazole
7	29.4	3	10	30.0	o-Methoxyphenol
7	29.5	3	15	20.0	Diethyl Propyl Amine
7	29.8	2	14	14.3	Diethylaminopropyne
7	29.8	3	9	33.3	4-Methyl Hexanoic Acid
7	30.0	4	11	36.4	i-Propyl Carbonate
7	30.6	2	13	15.4	3-Cyclohexene-1-Methanol
7	30.6	2	11	18.2	o,a-Dichlorotoluene
7	30.6	3	11	27.3	1-Ethoxy-1-Propoxyethane
7	30.6	3	9	33.3	3-Ethylpentane
7	30.7	2	16	12.5	Indazole
7	30.8	3	15	20.0	i-Amyl Acetate
7	31.1	1	13	7.7	Ethylidinecyclopentane
7	31.1	2	16	12.5	Cyclopentylacetate
7	31.2	3	12	25.0	Dicyclopropyl Ketone
7	31.3	4	11	36.4	n-Propyl Capronate
7	31.4	2	13	15.4	n-Propyl Acetothioacetate
7	31.5	2	13	15.4	Vinyl t-Amyl Ether
7	31.5	2	13	15.4	2-Furanacrylene
7	31.5	4	10	40.0	Bicyclo(2,2,1)-2,5-Heptadiene
7	31.6	2	10	20.0	3-Ethyl-3-Pentanol
7	31.6	2	10	20.0	Tetrahydrofurfuryl Acetate
7	31.6	3	11	27.3	5-Methyl-3-Hexanone
7	31.7	4	8	50.0	4,4-Dimethyl-1-Pentene
7	31.9	2	11	18.2	m-Chlorotoluene
7	31.9	4	10	40.0	Dipropyleneglycol Methyl Ether
7	32.4	2	11	18.2	p-Toluidine Hydrochloride
7	32.4	2	10	20.0	3,3-Dimethylpentane
7	32.5	1	13	7.7	2-Methyl-5-Hexanol
7	33.2	3	11	27.3	2-Ethylpyridine
7	33.4	3	8	37.5	Ethyl o-Formate
7	33.4	4	8	50.0	ar,ar-Dichlorotoluene
7	33.5	3	10	30.0	Ethyl-2-Methyl-3-Ketobutyrate
7	33.6	3	10	30.0	4-Heptanol
7	33.7	1	14	7.1	1-Ethylcyclopentene
7	33.7	2	15	13.3	i-Propyl Acetoacetate
7	33.7	2	13	15.4	2,2-Bis(Ethylmercapto) Propane
7	34.1	3	10	30.0	4-Heptanone
7	34.2	2	8	25.0	o-Fluorotoluene
7	34.3	2	11	18.2	Toluene
7	34.4	4	9	44.4	Trifluorotoluene
7	34.7	3	4	75.0	2-Propen-1,1-diol Diacetate
7	34.9	2	10	20.0	3-Methyl-2-Hexanol
7	35.3	2	15	13.3	Heptalactone
7	35.3	3	12	25.0	1,6-Heptadiyne
7	35.4	2	12	16.7	1,3-Bis(dimethylamino)-2-Propanol
7	35.4	4	8	50.0	n-Butyl Propionate
7	35.6	3	9	33.3	n-Butyl Acrylate
7	35.7	2	14	14.3	Methyl 2-Methylfuran-3-Carboxylate
7	35.7	3	12	25.0	Benzamide
7	36.0	2	12	16.7	p-Chlorotoluene
7	36.0	2	8	25.0	1,3,5-Cycloheptatriene
7	36.3	2	8	25.0	Di-n-Propyl Carbonate
7	36.5	3	8	37.5	2-Methyl-3-Hexanone
7	37.8	1	11	9.1	sec-Butyl Acrylate
7	38.4	3	7	42.9	Ethylene Dimethacrylate
7	38.4	2	3	66.7	m-Fluorotoluene
7	38.8	3	12	25.0	Trimethylpyrazine
7	38.9	1	10	10.0	2-Methyl-2-Hexanol
7	39.2	2	3	66.7	p-Fluorotoluene
7	39.3	2	12	16.7	2,3-Dimethyl-2-Pentanol
7	40.0	1	11	9.1	Norbornylene
7	40.4	3	8	37.5	p-Chlorobenzonitrile
7	40.8	2	7	28.6	p-Hydroxybenzoic Acid
7	41.0	2	9	22.2	5-Methyl-2-Hexanone
7	41.2	2	7	28.6	2-Heptanone
7	41.8	2	9	22.2	Benzonitrile
7	41.9	1	6	16.7	Cyclohexyl Methyl Amine
7	42.0	1	8	12.5	3-Ethylcyclopentene
7	42.1	2	8	25.0	3,3-Dimethylcyclobutane-carbonitrile
7	42.7	1	9	11.1	1-i-Propoxy-2-Methyl-2-Propanol
7	42.8	2	10	20.0	Methyl 3-Methylfuran-2-Carboxylate
7	43.0	1	13	7.7	Benzyl Chloride
7	43.0	2	8	25.0	Allyl Crotonate
7	43.1	1	7	14.3	2-Methylbutyl Acetate
7	43.4	2	7	28.6	sec-Butyl Propionate
7	43.5	2	8	25.0	t-Butyl Propionate
7	44.4	2	8	25.0	2,4-Dimethyl-3-Pentanone
7	44.8	2	6	33.3	2-n-Propylthiophene
7	45.2	1	8	12.5	2-Heptanol
7	45.7	2	12	16.7	o-Chlorotoluene
7	47.6	2	7	28.6	2-Furyl Ethyl Ketone
7	47.7	2	8	25.0	1,2-Dimethylpropyl Acetate
7	49.9	1	6	16.7	1,3-Propanediol Diacetate
7	50.0	2	7	28.6	Furfuryl Thioacetate
7	56.1	1	7	14.3	Allylidene Acetate
7	58.3	1	6	16.7	2-Amino-4-Methyl-n-Hexane
7	61.2	1	6	16.7	Proline Ethyl Ester
8	8.1	16	40	40.0	o-Methoxybenzoic Acid
8	9.0	12	44	27.3	9-Methyl-1,3,6-Trioxadecolin
8	9.1	13	30	43.3	2-Ethoxy-4-Methyl-tetrahydropyran
8	9.3	14	36	38.9	2-Carboethoxy-cyclopentanone
8	9.3	14	30	46.7	Octylmercaptane

C	Σ_g	N25	N5	R	Compound
8	9.5	13	37	35.1	3-Cyclohexene-1,1-Demethylol
8	9.7	10	30	33.3	2-Octenal
8	9.7	14	34	41.2	Caprylyl Chloride
8	9.8	12	30	40.0	Ethyl 4-Methylpentanoate
8	9.8	16	27	59.3	Methyl o-n-Valerate
8	9.9	14	21	66.7	2-Amino-6-Methylheptane
8	10.1	8	42	19.0	Ethyl-2-Hexenoate
8	10.1	14	30	46.7	2-Thianonane
8	10.1	16	32	50.0	1-Methyl-3-Cyclohexen-1-Carboxaldehyde
8	10.2	9	38	23.7	2-Ethyl-2-Hexen-1-ol
8	10.3	11	30	36.7	Ethyl-p-Quinone
8	10.3	13	24	54.2	i-Octanol
8	10.4	11	30	36.7	2-Octyne
8	10.6	12	22	54.5	Heptyl Formate
8	10.7	11	28	39.3	n-Octanol
8	10.7	11	22	50.0	6-Methylheptanol
8	10.8	9	35	25.7	Ethyl Sorbate
8	10.9	13	19	68.4	1-Octanol
8	11.1	13	26	50.0	1-Octanethiol
8	11.2	12	29	41.4	1-Octyne
8	11.2	10	23	43.5	2-Methyl-2-Heptenal
8	11.2	11	22	50.0	1,4-Diethoxybutane
8	11.3	9	32	28.1	Vanillin
8	11.6	8	25	32.0	4,4-Dimethyl-2-Penten-2-al
8	11.6	13	25	52.0	Cyclooctane
8	11.8	11	27	40.7	Cyclooctene
8	11.9	9	29	31.0	3-Octyne
8	12.0	9	31	29.0	p-Methylbenxyl Alcohol
8	12.0	9	29	31.0	4,4-Dimethyl-1,5-Hexadiene
8	12.2	9	30	30.0	Methyl Cyclohexane-carboxylate
8	12.3	10	30	33.3	1,4-Dimethylenecyclohexene
8	12.3	12	30	40.0	2,6-Dimethylcyclohexanol
8	12.3	7	17	41.2	2-Chlorooctane
8	12.4	8	38	21.1	7-Thiabicyclo(4.3.0) Nonane
8	12.5	11	31	35.5	1-Methanol-4-Methylene-cyclohexane
8	12.6	10	26	38.5	2-Thia-3-Methyl Octane
8	12.7	10	20	50.0	1-Octene
8	12.8	5	37	13.5	Isatin
8	12.8	11	27	40.7	4-Octyne
8	12.8	11	23	47.8	1-Methyl-2-Ethyl-cyclopentane
8	12.9	9	21	42.9	4-Octanol
8	13.0	11	27	40.7	1,2-Dimethylcyclohexene
8	13.0	11	24	45.8	1-Chlorooctane
8	13.1	12	20	60.0	4-n-Butoxy-n-Butanol
8	13.2	11	20	55.0	n-Propyl-n-Pentanoate
8	13.2	13	21	61.9	n-Propylcyclopentane
8	13.3	11	30	36.7	2-Octen-1-ol
8	13.3	10	20	50.0	1,1,3-Trimethylcyclopentane
8	13.4	8	27	29.6	2,3-Dihydro-2,5-Dimethylpyran-2-Methylol
8	13.4	12	20	60.0	2,5-Diethoxy Tetrahydrofuran
8	13.5	11	17	64.7	3-Ethyl-3-Hexanol
8	13.6	10	27	37.0	Ethyl Nicotinate
8	13.6	9	19	47.4	1,1-Diethoxy-2-Methylpropane
8	13.8	9	23	39.1	2-Ethyl-1-Hexanethiol
8	13.8	11	18	61.1	2-Methyl-3-Ethyl-3-Pentanol
8	13.9	10	17	58.8	4-Octanone
8	14.0	7	34	20.6	3-Thiabicyclo(4.3.0) Nonane
8	14.0	6	29	20.7	1-(3-Thenyl)-2-Butene
8	14.1	10	21	47.6	2,4-Dimethyl-3-hexanol
8	14.3	3	20	15.0	1,1-Diethyoxybutane
8	14.3	5	28	17.9	1-(2-Thenyl)-2-Butene
8	14.3	8	28	28.6	1,4-Benzenedicarbinol
8	14.4	8	19	42.1	1,3,7-Octatrien-5-yne
8	14.6	8	24	33.3	2-Cyclohexylvinylchloride
8	14.6	10	21	47.6	2-Octene
8	14.8	5	29	17.2	o-Methoxybenzaldehyde
8	14.8	9	22	40.9	Methyl-3-Methyl-4-Hexanoate
8	14.8	11	22	50.0	1-Methyl-3-Ethylcyclopentane
8	14.9	9	22	40.9	2,5-Dimethyl-1,5-Hexadiene
8	14.9	8	19	42.1	2-Ethyl-1-Hexanethiol
8	15.0	6	26	23.1	Ethyl-3-Hexanoate
8	15.0	9	21	42.9	Octalene Glycol
8	15.1	9	16	56.3	1,1,1-Triethoxyethane
8	15.2	10	25	40.0	1,3-Cyclooctadiene
8	15.2	10	20	50.0	1,1,2-Trimethylcyclopentane
8	15.4	5	27	18.5	1,4-Diethoxy-2-Butene
8	15.4	7	23	30.4	1,7-Octadiene
8	15.5	11	21	52.4	Benzyl Formate
8	15.7	7	22	31.8	Ethyl 2,3-Methylbutyrate
8	15.8	7	22	31.8	1,3,6-Octatriene
8	15.9	11	20	55.0	1,2-Dimethylcyclohexane
8	16.0	8	24	33.3	Methylformanalide
8	16.1	7	18	38.9	2-Methyl-5-Heptanone
8	16.1	7	16	43.8	Cyclohexyl Acetic Acid
8	16.2	7	21	33.3	Ethyl 2-Ketocyclopentancarboxylate
8	16.2	8	23	34.8	p-Cresyl Methyl Ether
8	16.3	8	15	53.3	3-Octanone
8	16.3	8	15	53.3	6-Methyl-3-Heptanone
8	16.4	7	24	29.2	2,5-Dimethyl-2,4-Hexadiene
8	16.4	8	20	40.0	3-Hepten-3-al
8	16.5	7	20	35.0	Butyl Methallyl Ether
8	16.7	7	20	35.0	Caprylic Acid
8	16.7	8	17	47.1	Propyl i-Valerate
8	16.7	10	13	76.9	t-Butyl 3-Ketobutyrate
8	16.8	5	17	29.4	o-Toluic Acid
8	16.8	9	19	47.4	4-Methyl-3-Heptanol
8	16.8	8	15	53.3	2-Methyl-3-Heptanone
8	16.9	8	18	44.4	Methyl Cyclohexyl Ketone
8	17.0	9	17	52.9	1,6-Octadiene
8	17.1	5	22	22.7	3-Cyclohexenyl Methyl Ketone
8	17.1	5	22	22.7	3-Octen-1-ol
8	17.1	8	16	50.0	4-Methyl-3-Heptanone
8	17.2	6	27	22.2	Spiro (5,5) 1,3,9-Trioxaundecane
8	17.3	10	18	55.6	4-Octene
8	17.4	5	23	21.7	1-Ethynylcyclohexanol
8	17.4	7	27	25.9	2-Thiahexahydroindan
8	17.5	6	19	31.6	2-Methyl-3-Heptene
8	17.6	5	25	20.0	2,3-Dimethylphenol
8	17.6	6	23	26.1	1,5-Cyclooctadiene
8	17.6	6	19	31.6	3-Propenylcyclopentane
8	17.6	7	19	36.8	2-Ethylhexanediol-1,3
8	17.9	7	19	36.8	Terephthalaldehydic Acid
8	17.9	6	16	37.5	2-(2-Butoxyethoxy) Ethanol
8	17.9	7	16	43.8	i-Propylcyclopentane
8	18.0	9	18	50.0	2,2,4-Trimethyl-4-Penten-1-ol
8	18.1	5	29	17.2	o-Vanillin
8	18.1	6	21	28.6	1,2-Dimethoxybenzene
8	18.2	4	31	12.9	Methyl 2-Hydroxy-cyclohexanecarboxylate
8	18.2	5	23	21.7	2,6-Dimethylphenol
8	18.2	7	19	36.8	2,3-Dimethyl-2-Hexene
8	18.3	4	21	19.0	Phenylacetonitrile
8	18.3	8	19	42.1	2,6-Dimethyl-4-Thiaheptane
8	18.5	7	18	38.9	Cyclooctatetraene
8	18.7	6	20	30.0	3,5-Dimethyl-3-Hexanol

C	Σ_g	N25	N5	R	Compound
8	18.7	6	17	35.3	2,3,4-Trimethyl-3-Penten-1-ol
8	18.8	4	22	18.2	p-Methoxybenzoic Acid
8	18.8	6	16	37.5	2,3,4-Trimethyl-2-Pentene
8	18.9	5	18	27.8	1,3-Dimethylcyclohexane
8	18.9	8	13	61.5	n-Butyl-i-Butyrate
8	19.0	5	18	27.8	Ethyl 2-Methylvalerate
8	19.1	4	20	20.0	Chlorostyrene
8	19.1	6	15	40.0	Terephthalaldehyde
8	19.1	6	13	46.2	2-Ethylhexanal
8	19.2	4	14	28.6	2-Hydroxy-3-Methylbenzoic Acid
8	19.2	7	17	41.2	2-Methyl-3-Heptanol
8	19.3	5	16	31.3	n-Butyl-n-Butyrate
8	19.4	3	26	11.5	n-Methyl-o-Toluidine
8	19.5	9	20	45.0	sec-Butyl Acetoacetate
8	19.6	6	21	28.6	2,5-Dimethyl-3-Pyrazine
8	19.8	4	20	20.0	Methyl 2,5-Dimethylfuran-3-Carboxylate
8	19.8	5	18	27.8	p-Tolualdehyde
8	19.8	6	19	31.6	2,3-Octanediol
8	19.9	3	19	15.8	1-Thiaindan
8	20.0	5	18	27.8	1,1-Dimethylcyclohexane
8	20.1	4	19	21.1	1,4-Dimethylcyclohexane
8	20.1	6	15	40.0	Methyl Salicylate
8	20.2	6	16	37.5	3,5-Dimethyl-4-Thiaheptane
8	20.3	3	23	13.0	1-(2-Butoxyethoxy) Ethanol
8	20.3	4	21	19.0	3,5-Dimethylcyclohexanol
8	20.3	4	14	28.6	2-Ethyl-1-Hexene
8	20.4	6	21	28.6	Ethylidenecyclohexene
8	20.4	6	11	54.5	3,4-Dimethylhexane
8	20.5	7	18	38.9	1-Methylene-4-Cyclohexane
8	20.6	4	17	23.5	Benzyl Methyl Ether
8	20.6	4	14	28.6	2,4,4-Trimethyl-2-Pentene
8	20.6	6	17	35.3	o-Methylbenzyl Alcohol
8	20.6	6	16	37.5	Bis(2-Ethoxyethyl) Ether
8	20.6	6	15	40.0	3,4,4-Trimethyl-2-pentene
8	20.7	7	17	41.2	3-Octanol
8	20.8	4	20	20.0	Ethyl 3-Ketocaproate
8	20.8	2	8	25.0	m-Chloroethylbenzene
8	20.9	6	20	30.0	p-Phenylene Diisocyanate
8	20.9	6	19	31.6	p-(Hydroxymethyl) Chlorobenzene
8	20.9	7	16	43.8	2,2-Dimethyl-3-Hexene
8	21.0	4	13	30.8	m-Aminoacetophenone
8	21.0	6	19	31.6	4-Ethenyl-1-Cyclohexene
8	21.0	5	14	35.7	Allyl i-Valerate
8	21.0	7	17	41.2	n-Butyl Acetoacetate
8	21.1	4	18	22.2	3,4-Dimethylphenol
8	21.1	5	16	31.3	i-Amyl Propionate
8	21.1	6	16	37.5	Furfuryl Propionate
8	21.2	4	13	30.8	Phenoxyacetic Acid
8	21.3	8	12	66.7	3-Methylheptane
8	21.4	2	23	8.7	o-Fluorophenetole
8	21.4	3	20	15.0	2-Hexyloxyethanol
8	21.4	4	20	20.0	3-Ethyl-5-Methylpyridine
8	21.5	5	16	31.3	1-Methyl-1-Ethylcyclopentane
8	21.5	5	13	38.5	Di-i-Butyl Sulfide
8	21.6	3	24	12.5	3,4-Dimethylchlorobenzene
8	21.6	3	11	27.3	p-Methoxybenzaldehyde
8	21.7	3	17	17.6	Cyclohexyl Acetate
8	21.9	5	17	29.4	m-Tolualdehyde
8	21.9	6	13	46.2	2,4-Dimethylhexane
8	22.0	4	13	30.8	o-Tolualdehyde
8	22.0	5	14	35.7	2-Ethyl-1,3-Hexanediol
8	22.2	5	22	22.7	2,3,5-Trimethylpyridine
8	22.2	4	16	25.0	Ethylcyclohexane
8	22.3	5	14	35.7	2-Cyclohexylethanol
8	22.4	3	17	17.6	Allyl Tiglate
8	22.4	4	15	26.7	1,7-Octadiene
8	22.4	4	15	26.7	Triethyl o-Acetate
8	22.6	5	17	29.4	4-Methyl-4-Heptanol
8	22.7	4	16	25.0	2,4-Dimethyl-3-Ethylpyrrole
8	22.7	7	14	50.0	sec Butyl Ether
8	22.9	5	17	29.4	Ethyl 4-Methyl-3-Ketovalerate
8	23.1	3	14	21.4	2,4-Xylenol
8	23.2	4	18	22.2	Methyl Heptanoate
8	23.3	3	17	17.6	2,3,6-Trimethylpyridine
8	23.4	3	19	15.8	Phthalaldehydic Acid
8	23.6	3	19	15.8	i-Vanillin
8	23.6	6	12	50.0	2-Methylheptane
8	23.7	5	15	33.3	Styrene Oxide
8	23.7	6	14	42.9	2-Ethyl-1-Hexanol
8	23.8	3	19	15.8	1-Ethylcyclohexene
8	23.9	3	11	27.3	p-Toluic Acid
8	23.9	4	11	36.4	2,5-Dimethylhexane
8	24.0	4	17	23.5	1,2,3-Trimethylcyclopentane
8	24.0	4	16	25.0	Piperonal
8	24.0	5	14	35.7	2,3-Dimethyl-3-Hexanol
8	24.1	3	15	20.0	1-(2-Chlorophenyl) Ethanol
8	24.1	3	14	21.4	p-Cyanobenzoic Acid
8	24.2	4	14	28.6	Styrene Glycol
8	24.2	7	9	77.8	Trimethyl o-Valerate
8	24.3	6	16	37.5	2,2,4-Trimethyl-1,3-Pentanediol
8	24.3	7	14	50.0	3-Methyl-3-Heptanol
8	24.4	3	17	17.6	Anisaldehyde
8	24.4	5	13	38.5	3,5-Dimethyl-3-Hexanol
8	24.5	2	19	10.5	2-Methyl-5-Ethenylpyridine
8	24.5	3	11	27.3	3,5-Xylenol
8	24.7	4	15	26.7	sec-Butyl Methacrylate
8	25.0	5	21	23.8	Ethyl 2-Ethyl-3-Ketobutyrate
8	25.1	3	15	20.0	1,2,4-Trimethylcyclopentane
8	25.1	4	11	36.4	1,1-Dipropoxyethane
8	25.1	6	15	40.0	n-Octane
8	25.4	4	15	26.7	t-Butyl Acetoacetate
8	25.4	4	14	28.6	o-Chloroethylbenzene
8	25.4	4	11	36.4	2,5-Dimethyl-2,5-Hexanediol
8	25.6	5	13	38.5	3,3-Dimethylhexane
8	25.7	2	13	15.4	2-(o-Chlorophenyl) Ethylamine
8	25.7	3	18	16.7	3-Ethyl-4-Methylpyridine
8	25.8	3	13	23.1	2,5-Xylenol
8	25.9	4	14	28.6	Di-n-Butylamine
8	25.9	4	11	36.4	Phthalic Anhydride
8	26.0	2	14	14.3	2,5-Dimethyl-2-Hexene
8	26.0	4	13	30.8	n-Amyl Propionate
8	26.1	3	18	16.7	Tetrahydro-2,2,4,4-Tetramethyl-3-Furanol
8	26.1	4	13	30.8	3-Ethyl-2-Methyl-1-Pentene
8	26.2	2	16	12.5	2-Methyl-5-Ethylpyridine
8	26.3	4	13	30.8	Di-i-Butylamine
8	26.4	5	12	41.7	n-Butyl Methacrylate
8	26.5	2	16	12.5	4-Methyl-5-Heptanol
8	26.5	3	13	23.1	2-Methylbenzothiazole
8	26.5	4	14	28.6	p-Chloroethylbenzene
8	26.5	4	12	33.3	i-Butyl Methacrylate
8	26.6	3	13	23.1	1,2-Octanediol
8	26.6	4	10	40.0	Tetramethylpyrazine
8	26.6	6	11	54.5	2,3,3-Trimethylpentane
8	26.7	3	15	20.0	1-Methylbutyl Propionate
8	26.9	3	12	25.0	m-Toluic Acid
8	26.9	4	10	40.0	2,3-Dimethylhexane
8	27.0	3	12	25.0	3-Pyridylathyl Ketone
8	27.1	3	17	17.6	2-Ethyl-1-Hexanol
8	27.3	4	15	26.7	2-Methyl-6-Ethylpyridine
8	27.4	2	14	14.3	p-Anisic Acid

C	Σ_g	N25	N5	R	Compound
8	27.4	3	18	16.7	1-Methanol-4-Methyl-cyclohexane
8	27.4	4	11	36.4	m-Hydroxyacetophenone
8	27.5	4	10	40.0	4-Methylheptane
8	27.6	4	13	30.8	Amyl Lactone
8	27.6	4	11	36.4	p-Chloroacetophenone
8	27.6	4	10	40.0	m-Chloroacetophenone
8	27.7	4	11	36.4	Phenyl Methyl Ketone
8	27.7	5	13	38.5	2,3,4-Trimethyl-3-Pentanol
8	27.8	2	11	18.2	Dimethyl Aniline
8	27.9	2	16	12.5	2-Methyl-5-Ethylpyridine
8	27.9	3	15	20.0	Benzylcyanide
8	28.0	3	14	21.4	Di-sec-Butyl Amine
8	28.1	3	15	20.0	Acetylaldehyde Dipropargyl Acetal
8	28.4	2	15	13.3	m-Methoxybenzoic Acid
8	28.6	3	11	27.3	2-Methyl-3-Ethylpentane
8	28.7	2	11	18.2	3-t-Butylthiophane
8	28.7	3	13	23.1	o-Chloroacetophenone
8	28.8	3	13	23.1	o-Tolunitrile
8	28.8	3	13	23.1	m-Tolunitrile
8	28.9	1	17	5.9	2-Amino-5-Methylheptane
8	28.9	3	15	20.0	1,3,7-Octatriene
8	28.9	3	9	33.3	Acetophenone
8	29.2	3	13	23.1	p-Tolunitrile
8	29.3	2	17	11.8	2-Ethyl-3-Hexen-1-ol
8	29.4	2	15	13.3	n-Ethylanaline
8	29.5	3	10	30.0	2,3,4-Trimethylpentane
8	29.6	2	11	18.2	i-Propyl Furoate
8	29.7	3	12	25.0	1,3-Dimethylbenzene
8	29.7	3	12	25.0	p-Fluorostyrene
8	29.7	4	13	30.8	2,2,4,4-Tetramethyl-tetrahydrofuran
8	29.8	2	14	14.3	N-Ethyl Cyclohexylamine
8	29.9	3	17	17.6	1,4-Dimethylbenzene
8	29.9	3	11	27.3	Tetrahydrophthalic Anhydride
8	30.0	2	17	11.8	Bis(2-Vinyloxyethyl) Ether
8	30.0	3	13	23.1	a-Chlorophenetole
8	30.1	2	9	22.2	2-Methyl-2-Heptanethiol
8	30.1	4	12	33.3	2,2,5,5-Tetramethyl-tetrahydrofuran
8	30.2	2	10	20.0	Difluorostyrene
8	30.2	3	9	33.3	N,N-Butylpyrrole
8	30.3	1	11	9.1	2-t-Butylthiophene
8	30.3	3	13	23.1	1-(2-Ethoxypropoxy)-i-Propanol
8	30.4	3	12	25.0	ar-Methoxybenzaldehyde
8	30.5	4	8	50.0	3-Methyl-3-Ethylpentane
8	30.7	3	11	27.3	2-Methylbutyl Propionate
8	30.7	5	13	38.5	i-Butyl Acetoacetate
8	30.9	4	17	23.5	2-Propyl-4-Methylfuran
8	31.0	2	12	16.7	2-Chloro-p-Xylene
8	31.0	2	8	25.0	2-Thiaindan
8	31.0	4	11	36.4	3-Octylamine
8	31.0	4	8	50.0	Methyl Benzoate
8	31.1	4	11	36.4	i-Butyric Anhydride
8	31.2	2	13	15.4	3-Acetyl-2,4-Dimethylpyrsole
8	31.3	2	11	18.2	Bicyclo (3.3.0) Octane
8	31.5	2	14	14.3	6-Methyl-2-Heptanone
8	31.6	2	16	12.5	1,2-Dimethylbenzene
8	31.6	3	10	30.0	2,4,4-Trimethyl-1-pentene
8	31.9	2	11	18.2	Indole
8	32.0	3	10	30.0	n-Butyl Crotonate
8	32.2	2	13	15.4	3-Ethylhexane
8	32.4	4	11	36.4	Di-n-Propyl Acetal
8	32.6	1	14	7.1	Butyl Tetrahydrothiophene
8	32.8	2	9	22.2	2,5-Diethylthiophene
8	32.8	3	7	42.9	Methyl p-Aminobenzoate
8	33.4	2	13	15.4	1,4-Dioxaspiro(4,5) Decane
8	33.4	3	8	37.5	Di-i-Butylene
8	33.5	3	6	50.0	1-Ethyl-4-Fluorobenzene
8	33.7	2	12	16.7	n-Hexyl Acetate
8	34.0	3	8	37.5	2,2,3-Trimethylpentane
8	34.5	2	7	28.6	m-Propyl Furoate
8	34.6	2	9	22.2	Tetrahydro-2,5-Dimethylpyran-2-Methylol
8	34.6	3	11	27.3	p-Chlorophenetole
8	34.6	3	8	37.5	Phthalide
8	34.7	3	11	27.3	o-Chlorophenetole
8	34.8	2	10	20.0	Ethyl Phenyl Ether
8	34.8	3	8	37.5	Hydroxy-o-Toluic Acid
8	35.5	1	12	8.3	2-Hexenyl Acetate
8	35.5	3	11	27.3	i-Leucine Ethyl Ester
8	35.7	1	12	8.3	2-Octanol
8	35.7	2	8	25.0	o-Hydroxyacetophenone
8	35.9	2	11	18.2	p-Ethylphenol
8	35.9	3	8	37.5	4,4-Dimethyl-1-Penten-2-al
8	36.0	3	12	25.0	2-Amino-n-Octane
8	36.2	2	8	25.0	2-Octanone
8	36.3	2	11	18.2	1-Methylbicyclo(2.2.1) Heptene
8	36.4	1	12	8.3	2,6-Octadiene
8	36.4	2	8	25.0	2-n-Butyltetrahydrofuran
8	36.9	1	10	10.0	1-Chloro-2-Ethylhexane
8	37.0	2	11	18.2	Octalactone
8	37.0	5	10	50.0	2-Phenoxyethanol
8	37.4	2	10	20.0	3-Hexen-1-yl Acetate
8	37.6	1	9	11.1	2,3-Benzothiophene
8	38.0	2	11	18.2	2,5-Dimethyl-2-Hexanol
8	38.0	3	6	50.0	p-Hydroxyacetophenone
8	38.4	1	12	8.3	2-Methyl-2-Heptanol
8	38.7	3	6	50.0	1-Phenyl-1,2-Dihydroxyethane
8	38.8	3	10	30.0	sec-Butyl Crotonate
8	38.8	2	6	33.3	alpha-(Chloromethyl) Benzyl Alcohol
8	39.0	3	11	27.3	n-Leucine Ethyl Ester
8	39.1	2	7	28.6	2-Phenyl Ethanol
8	39.3	2	8	25.0	1-Phenyl-2-Thiapropane
8	39.5	2	7	28.6	o-Ethylphenol
8	39.8	2	10	20.0	(p-Chlorophenyl) Acetylene
8	39.8	3	7	42.9	2,2,4-Trimethylpentane
8	40.3	2	5	40.0	Methyl p-Hydroxybenzoate
8	40.9	3	8	37.5	2,2-Dimethylhexane
8	41.0	2	13	15.4	Ethyl-1,3-Dimethyl-butylamine
8	41.3	2	5	40.0	m-Ethylphenol
8	41.6	3	8	37.5	Benzofuran
8	41.8	3	8	37.5	2,2,3,3-Tetramethylbutane
8	42.1	2	6	33.3	t-Butyl-i-Butyl Ether
8	42.2	2	7	28.6	p-Ethoxyphenol
8	42.4	2	9	22.2	Ethylbenzene
8	43.3	1	6	16.7	2-n-Butylthiophene
8	43.7	2	6	33.3	p-Fluorophenetole
8	44.0	2	7	28.6	2-i-Butylthiophene
8	45.1	1	9	11.1	Phenylacetylene
8	45.3	1	10	10.0	4-Hydroxyoctanoic Acid Lactone
8	45.3	1	8	12.5	1,4-Dicyanobenzene
8	46.1	1	8	12.5	1,2-Dicyanobenzene
8	46.1	2	5	40.0	Phenyl Acetic Acid
8	46.8	1	5	20.0	n-Butyl Ether
8	47.0	1	10	10.0	(1-Chloroethyl) Benzene
8	47.3	2	4	50.0	m-Acetoxyphenol
8	47.6	2	7	28.6	2,2,4,4-Tetramethyl-3-Thiapentane
8	47.6	2	7	28.6	Di-t-Butyl Peroxide
8	47.8	1	7	14.3	t-Butyl Sulfide

C	Σ_g	N25	N5	R	Compound
8	48.0	1	9	11.1	N,N-Dimethyl Cyclohexylamine
8	49.0	1	8	12.5	t-Octylamine
8	49.4	1	9	11.1	2-Amino-2-Methylheptane
8	49.8	1	7	14.3	2-(Chloroethyl) Benzene
8	50.2	1	7	14.3	Phenyl Acetate
8	50.3	1	5	20.0	Dimethyl Aminoethyl Methacrylate
8	50.7	1	5	20.0	Styrene
8	51.2	2	5	40.0	Butyric Anhydride
8	54.8	1	6	16.7	Bis(2-Dimethylaminoethyl) Ether
8	56.6	1	3	33.3	1-Octylamine
8	59.0	1	7	14.3	Furfuryl i-Propylsulfide
8	59.0	1	4	25.0	Phenylethylamine
8	59.1	2	4	50.0	Phenyl Acetaldehyde
8	67.8	1	2	50.0	2-Octylamine
8	70.7	1	3	33.3	Di-s-Butyl Sulfide
9	7.7	13	50	26.0	Methyl 2-Octynoate
9	8.2	15	41	36.6	6-Nonenal
9	8.4	14	48	29.2	Methyl 2-Octenoate
9	8.5	17	44	38.6	Nonadienol
9	8.7	15	44	34.1	2-Thia-trans-Decahydronaphthalene
9	9.3	16	35	45.7	2,5-Dimethyl-3-n-Propylpiperazine
9	9.6	17	30	56.7	1,9-Nonanediol
9	9.7	13	32	40.6	2-Nonenal
9	10.1	13	34	38.2	2-i-Propylcyclohexanol
9	10.2	11	33	33.3	3,4-Dimethyl-4-Heptanol
9	10.2	13	22	59.1	1-Nonanol
9	10.6	12	27	44.4	5-Ethyl-2-Heptanol
9	10.7	13	31	41.9	Nonanal
9	10.7	12	27	44.4	n-Nonyl Aldehyde
9	11.1	10	29	34.5	2,3-Dimethyl Benzoic Acid
9	11.5	11	25	44.0	2-Methyl-3-Octanol
9	11.6	11	22	50.0	1-Nonyne
9	11.9	10	29	34.5	1,8-Nonadiyne
9	12.0	11	28	39.3	Ethyl Heptoate
9	12.1	8	29	27.6	Dimethylbenzyl Hydroperoxide
9	12.1	10	27	37.0	1-Nonanethiol
9	12.1	12	26	46.2	Hexahydroindan
9	12.2	12	22	54.5	i-Butylcyclopentane
9	12.5	12	24	50.0	1,2,3-Trimethylcyclohexane
9	12.6	9	30	30.0	2-Thia-1,2,3,4-Tetrahydronaphthalene
9	12.6	11	26	42.3	1,2,4-Trimethylcyclohexane
9	12.7	11	23	47.8	n-Butylcyclopentane
9	13.1	7	33	21.2	2-Thiatricyclo (3.3.1.1.3.7) Decane
9	13.1	8	23	34.8	4-Nonanol
9	13.1	9	21	42.9	1,1,3,4-Tetramethyl-cyclopentane
9	13.1	10	22	45.5	2,4-Dimethylbenzyl Alcohol
9	13.3	7	26	26.9	Cinnamyl Alcohol
9	13.3	10	30	33.3	3-Nonyne
9	13.4	8	28	28.6	Cinnamic Acid
9	13.5	10	24	41.7	1-Nonene
9	13.8	8	26	30.8	n-Octyl Formamide
9	13.9	11	24	45.8	1,1-Diethoxy-2-Methylbutane
9	13.9	10	18	55.6	1,1,3,3-Tetramethyl-cyclopentane
9	14.0	8	22	36.4	2,5-Dimethylbenzoic Acid
9	14.0	8	22	36.4	1,1-Diethoxy-3-Methyl-3-Butene
9	14.0	10	23	43.5	1,1,2-Trimethylcyclohexane
9	14.2	11	20	55.0	4,4-Dimethyl-3-Ethyl-2-Pentene
9	14.3	12	26	46.2	1-Methyl-1,3-Dimethyl-5-Cyclohexanol
9	14.6	8	23	34.8	4-Methyl-4-Octanol
9	14.6	8	21	38.1	3-Methyl-2-Propylpentanol
9	14.6	9	21	42.9	2,6-Dimethyl-4-Heptanol
9	14.6	9	21	42.9	1,1-Diethoxypentane
9	14.7	7	20	35.0	n-Butyl i-Valerate
9	14.8	7	22	31.8	3,5-Dimethylbenzyl Alcohol
9	15.2	7	21	33.3	AR-Vinylbenzyl Alcohol
9	15.2	8	24	33.3	ar-Ethylbenzyl Alcohol
9	15.2	10	20	50.0	1,1-Diethoxy-3-Methylbutane
9	15.3	8	25	32.0	2,6-Dimethylbenzoic Acid
9	15.4	7	25	28.0	3,4-Dimethylbenzoic Acid
9	15.4	7	17	41.2	2-Cyclohexylethyl Methyl Ether
9	15.5	7	20	35.0	Alpha Hydrindone
9	15.6	9	20	45.0	2,4-Dimethyl-4-Heptanol
9	15.6	12	24	50.0	2-Nonyne
9	15.7	9	18	50.0	n-Hexylpropionate
9	16.0	4	26	15.4	1-Thia-1,2,3,4-Tetrahydro-naphthalene
9	16.0	7	23	30.4	Nonanoic Acid
9	16.1	5	24	20.8	p-Chlorocumene
9	16.2	6	20	30.0	Allyl Caproate
9	16.3	8	19	42.1	N-Amyl Methacrylate
9	16.6	6	16	37.5	n-Butyl n-Valerate
9	16.7	9	20	45.0	2,6-Dimethyl-3-Heptanol
9	16.9	6	15	40.0	i-Butyl n-Valerate
9	16.9	8	19	42.1	3-Nonanol
9	17.0	7	22	31.8	1-Indanone
9	17.0	8	18	44.4	i-Amyl Butyrate
9	17.1	9	21	42.9	2,4-Dimethyl-3-Heptanol
9	17.3	8	23	34.8	4-Nonyne
9	17.6	9	12	75.0	3-Methyl-4-Ethylhexene
9	17.8	6	15	40.0	2-Methylpropyl i-Valerate
9	17.9	4	23	17.4	Nornicotine
9	17.9	7	23	30.4	2-Butyl-2-Ethyl-1,3-Propanediol
9	18.1	5	22	22.7	2,6-Nonedienal
9	18.2	5	16	31.3	i-Propylcyclohexane
9	18.2	6	19	31.6	1-Ethoxy-1-Pentoxyethane
9	18.2	6	15	40.0	5-Nonanone
9	18.2	6	12	50.0	3,3,4-Trimethylhexane
9	18.3	4	23	17.4	1-Methoxy-2-Phenoxyethane
9	18.3	8	20	40.0	4-Nonene
9	18.3	7	11	63.6	3,3-Dimethylheptane
9	18.4	6	18	33.3	i-Propenylbenzene
9	18.4	6	14	42.9	5-Nonanone
9	18.5	6	23	26.1	3,6-Dimethyl-3-Heptanol
9	18.5	4	13	30.8	1-Phenoxy-2-Propanone
9	18.6	5	17	29.4	1,1-Dimethylbutoxy-2-Propanol
9	18.9	4	27	14.8	Methyl 4-Methylcyclo-hexanecarboxylate
9	19.0	3	21	14.3	3,3,5-Trimethylcyclohexanol
9	19.0	5	21	23.8	Cumene Hydroperoxide
9	19.0	6	18	33.3	Phenyl 2-Propynyl Ether
9	19.1	6	12	50.0	Amyl Butyrate
9	19.1	8	14	57.1	3,4-Dimethylheptane
9	19.2	5	16	31.3	1,3,5-Trimethylcyclohexane
9	19.3	4	17	23.5	Phenyl Allyl Ether
9	19.6	5	22	22.7	o-Cresylethyl Ether
9	19.6	7	16	43.8	1,1-Dipropoxypropane
9	19.8	5	20	25.0	m-Cresylethyl Ether
9	19.8	6	18	33.3	1-Chlorononane
9	19.8	6	12	50.0	2,4,4-Trimethylhexane
9	20.0	5	15	33.3	i-Butyl i-Valerate
9	20.1	6	16	37.5	1,1,3-Trimethylcyclohexane
9	20.2	5	16	31.3	2,4-Dimethylbenzoic Acid
9	20.2	7	18	38.9	Methyl Caprylate

C	Σ_g	N25	N5	R	Compound
9	20.5	7	15	46.7	2,5-Dimethylbenzyl Alcohol
9	20.6	5	18	27.8	Methyl-4-Ethylcyclohexane
9	20.6	7	14	50.0	1-Phenyl-1-Methyl-1,2-Epoxyethane
9	20.8	4	23	17.4	A-Ethyl-p-Hydroxybenzyl Alcohol
9	20.8	7	12	58.3	2,6-Dimethyl-4-Heptanone
9	21.1	4	20	20.0	p-Cresylethyl Ether
9	21.2	4	16	25.0	AR-Ethylbenzaldehyde
9	21.3	5	16	31.3	Cinnamaldehyde
9	21.4	3	19	15.8	Chlorovinyltoluene
9	21.4	3	18	16.7	2-Thiabicyclo (4.4.0) Decane
9	21.5	5	18	27.8	o-Allylphenone
9	21.7	4	18	22.2	3-Phenyl-1-Propene
9	21.7	4	18	22.2	2,3-Dihydro-2-Methylbenzofuran
9	21.7	4	16	25.0	Dihydrocoumarin
9	21.8	4	16	25.0	3,4,4-Trimethyl-2-Hexene
9	22.0	5	12	41.7	2-(2,2-Dimethylpropyl) Thiophene
9	22.1	3	17	17.6	2,2-Difurylmethane
9	22.1	4	12	33.3	2,3-Dimethyl-3-Ethylpentane
9	22.2	4	16	25.0	n-Propylcyclohexane
9	22.2	5	15	33.3	Di-sec-Butoxymethane
9	22.3	3	23	13.0	2.6-Dimethyl-3-Ethylpyridine
9	22.3	5	14	35.7	3,5-Dimethylbenzoic Acid
9	22.4	5	12	41.7	3-Hepten-1-yl Acetate
9	22.5	3	23	13.0	3-Cyclohexylpropionic Acid
9	22.5	4	20	20.0	m-Methylstyrene
9	22.6	3	17	17.6	Methyl p-Tolyl Ketone
9	22.9	4	14	28.6	Methyl o-Toluate
9	22.9	5	16	31.3	i-Propyl Hexanoate
9	23.1	5	16	31.3	3,5,5-Trimethylhexanoic Acid
9	23.2	5	14	35.7	7-Methyl-4-Octanone
9	23.3	4	15	26.7	n-Nonane
9	23.3	6	17	35.3	o-2-Propylphenol
9	23.5	4	12	33.3	3,5,5-Trimethylcyclohexen-3-one
9	23.7	3	15	20.0	Ethyl Benzyl Ether
9	23.7	3	14	21.4	2-Methylbutyl i-Butyrate
9	23.7	3	9	33.3	3-Nonanone
9	23.8	3	19	15.8	4-6-Propylcyclohexanol
9	24.3	2	21	9.5	2,6-Dimethyl-4-Ethylpyridine
9	24.3	3	14	21.4	1-Methyl-1-Ethylcyclohexane
9	24.4	5	13	38.5	Benzyl Acetate
9	24.5	2	19	10.5	1-Methoxy-1-Hexoxyethane
9	24.6	3	22	13.6	2-t-Butyl-4-Methylfuran
9	24.7	5	13	38.5	4-Ethylheptane
9	24.8	3	13	23.1	2,4,6-Trimethylphenol
9	24.9	3	14	21.4	5-Methylphthalide
9	25.0	5	14	35.7	2-Methyl-4-Ethylhexane
9	25.1	5	13	38.5	5-Nonanol
9	25.2	5	13	38.5	Vinylbenzaldehyde
9	25.3	3	16	18.8	n-Heptyl Acetate
9	25.4	3	12	25.0	o-Methylacetophenone
9	25.5	4	17	23.5	n-None-2,4-Dienal
9	25.5	5	8	62.5	p-Methylacetophenone
9	25.6	2	12	16.7	2-Nonanone
9	25.6	3	18	16.7	2-Ethylbenzimidazole
9	25.7	4	16	25.0	2-(2-Methylallyloxy)-2-Methyl-1-Propanol
9	25.7	5	16	31.3	3-Methyl-3-Octanol
9	25.8	3	17	17.6	Triallylamine
9	25.8	4	12	33.3	4-Butoxy-3-Methyl-2-Butanone
9	26.0	2	12	16.7	6-Methylbenzo (B) Thiophene
9	26.0	4	20	20.0	2-Indanone
9	26.2	5	11	45.5	2,2,3,3-Tetramethylpentane
9	26.3	3	14	21.4	Cyclohexyl Acrylate
9	26.3	4	16	25.0	Coumarin
9	26.3	4	11	36.4	2,2,3,4-Tetramethylpentane
9	26.4	4	13	30.8	3-Ethylheptane
9	26.4	5	13	38.5	2-Methyloctane
9	26.5	5	12	41.7	3-Methyl-3-Ethylhexane
9	26.6	6	14	42.9	4-Nonanone
9	26.7	5	13	38.5	2,3,4-Trimethylhexane
9	26.8	3	15	20.0	o-Methylstyrene
9	26.8	3	12	25.0	2-Methyl-1-Octene
9	27.0	3	15	20.0	o-Methylphenetole
9	27.2	4	12	33.3	2,6-Dimethylheptane
9	27.4	2	14	14.3	5-Methyl-2,3-Benzothiophene
9	27.5	4	12	33.3	4,4-Dimethylheptane
9	27.7	2	14	14.3	5-Methyl Indole
9	27.8	3	14	21.4	3,5,5-Trimethyl-1-Hexanol
9	27.9	2	13	15.4	n-Ethyl-o-Toluidine
9	27.9	5	12	41.7	2,3,3-Trimethylhexane
9	28.4	5	13	38.5	4-Methyloctane
9	28.4	5	12	41.7	2-Methyl-3-Ethylhexane
9	28.5	2	14	14.3	4-Methyl-2,3-Benzothiophene
9	28.5	3	15	20.0	2,4-Dimethyl-6-Ethylpyridine
9	28.6	3	13	23.1	Hydrocinnamic Acid
9	28.6	5	12	41.7	2-Methyl-3-Octanone
9	28.7	2	15	13.3	Beta-Phenylethyl Formate
9	28.8	2	15	13.3	6-Methyl Indole
9	28.8	2	14	14.3	Chloromesitylene
9	28.8	4	12	33.3	2,5-Dimethylheptane
9	28.8	4	9	44.4	o-Chlorocumene
9	29.0	3	16	18.8	Methyl Octanoate
9	29.1	2	15	13.3	p-Cresyl Acetate
9	29.2	2	13	15.4	1,2,4-Trimethylbenzene
9	29.2	4	13	30.8	2,4-Dimethylheptane
9	29.3	2	16	12.5	ar-Ethylbenzyl Chloride
9	29.4	4	11	36.4	Styrene Glycol Methyl Ether
9	29.6	2	14	14.3	3-Chloroallyl Benzene
9	29.6	3	17	17.6	1-Methoxy-1-trans-Hexene-2-oxy Ethane
9	29.7	2	16	12.5	2,6-Dimethyl-2,5-Heptadien-4-one
9	29.8	2	14	14.3	2-Methyl Indole
9	29.8	4	13	30.8	2,6-Dimethyl-3-Heptanone
9	30.1	4	12	33.3	2,4-Dimethyl-3-Ethylpentane
9	30.1	5	13	38.5	2-(m-Tolyloxy) Ethanol
9	30.1	5	10	50.0	2,3,3,4-Tetramethylpentane
9	30.2	1	16	6.3	2-Phenyl Propynal
9	30.2	2	14	14.3	1,2,3-Trimethylbenzene
9	30.2	5	10	50.0	n-Amyl i-Butyrate
9	30.3	2	11	18.2	Indene
9	30.4	2	9	22.2	p-Dimethylamino-benzaldehyde
9	30.4	3	10	30.0	2,2-Dimethyl-3-Ethylpentane
9	30.7	2	9	22.2	1-Chloroindane
9	30.9	3	13	23.1	Tri-n-Propylamine
9	30.9	4	13	30.8	3-Methyloctane
9	31.0	3	10	30.0	AR-Methylacetophenone
9	31.1	3	13	23.1	2,3,5-Trimethylhexane
9	31.1	4	12	33.3	3,5-Dimethylheptane
9	31.3	1	16	6.3	2,4-Dimethyl-2,4-Heptadienal
9	31.6	1	13	7.7	2-Nonanol
9	31.6	4	12	33.3	2,3-Dimethylheptane
9	31.9	1	14	7.1	2,5-Dimethyl-3-n-Propylpyrazine
9	32.1	2	9	22.2	Methylphenylacetylene
9	32.3	3	10	30.0	2,2,3-Trimethylhexane
9	32.5	3	11	27.3	Methyl p-Toluate
9	32.5	3	10	30.0	Indane

C	Σ_g	N25	N5	R	Compound
9	32.9	2	13	15.4	3-Methyl Indole
9	33.0	2	12	16.7	1-Methylbutyl i-Butyrate
9	33.2	4	11	36.4	Di-n-Butoxymethane
9	33.3	3	10	30.0	2,2-Dimethylheptane
9	33.5	2	8	25.0	Phenyl-2-Propanone
9	33.7	4	6	66.7	Ethyl Benzoate
9	33.8	3	10	30.0	Methyl m-Toluate
9	34.0	2	10	20.0	2-Ethyl-5-n-Propylthiophene
9	34.2	1	16	6.3	Decahydroquinoline
9	34.2	1	14	7.1	Quinoline
9	34.2	1	14	7.1	gamma-Nonalactone
9	34.2	2	11	18.2	1,3,5-Trimethylbenzene
9	34.3	1	12	8.3	i-Quinoline
9	35.1	2	7	28.6	2-Methylbenzofuran
9	35.3	2	8	25.0	2-i-Amylthiophene
9	35.7	2	8	25.0	Phenylacetone
9	35.7	3	8	37.5	Di-i-Butoxymethane
9	36.1	3	9	33.3	p-Methoxyacetophenone
9	36.2	3	9	33.3	ar-Vinylbenzyl Chloride
9	36.6	1	9	11.1	2-Phenylpropanol
9	36.9	1	12	8.3	3-Cyclohexene-1-Carboxaldehyde Dimethyl Acetal
9	37.2	2	9	22.2	3-Chloropropenyl Benzene
9	37.6	1	11	9.1	(1-Chloroethyl) Toluene
9	37.7	1	14	7.1	3,5,5-Trimethylhexylamine
9	38.0	3	9	33.3	2,2,4-Trimethylhexane
9	38.5	2	8	25.0	1-Chloro-2-Propylbenzene
9	38.8	2	10	20.0	p-Methylphenethyl Alcohol
9	38.8	2	9	22.2	p-Ethyltoluene
9	38.9	2	11	18.2	i-Propylbenzene
9	39.0	2	9	22.2	3,3-Diethylpentane
9	39.5	2	9	22.2	6-Methylquinoxaline
9	40.0	2	6	33.3	p-2-Propylphenol
9	40.6	2	8	25.0	2,2,5-Trimethylhexane
9	41.0	2	9	22.2	5-Methylquinoxaline
9	41.3	2	6	33.3	1-Phenyl-1,2-Propanedione
9	41.8	2	8	25.0	m-Ethyltoluene
9	42.4	1	9	11.1	1-Methoxy-1-(cis-3-Hexenoxy) Ethane
9	42.6	1	9	11.1	(2-Chloropropyl) Benzene
9	43.5	1	8	12.5	Phenylpropionaldehyde
9	43.5	2	8	25.0	o-Ethyltoluene
9	44.2	1	9	11.1	2-Phenoxy-1-Propanol
9	44.2	2	6	33.3	(3-Chloropropyl) Benzene
9	44.3	1	8	12.5	1-Methoxy-1-cis-Hexane-3-Oxyethane
9	44.6	1	6	16.7	2-n-Pentylthiophene
9	45.4	2	5	40.0	Propiophenone
9	46.1	2	7	28.6	2,2,4,4-Tetramethylpentane
9	47.5	2	7	28.6	Santene
9	48.1	1	6	16.7	p-Propoxyphenol
9	51.3	2	6	33.3	Phenyl n-Propyl Ether
9	52.3	1	6	16.7	n-Propylbenzene
9	63.4	1	2	50.0	n-m-Butylpiperidine
10	7.5	16	48	33.3	3A,4,7,7A-Tetrahydro-4,7-Menthanoinden-1-ol
10	7.8	20	36	55.6	n-Decanal
10	8.2	14	45	31.1	Cinnamyl Methyl Ether
10	8.7	16	45	35.6	3-p-Tolylpropynal
10	8.9	12	45	26.7	Dipentene Oxide
10	8.9	14	52	26.9	2-Cyclopentylidene Cyclopentanone
10	9.0	15	28	53.6	1-Decanol
10	9.2	16	36	44.4	a-Pinene Oxide
10	9.5	11	37	29.7	2-Decenal
10	9.7	11	36	30.6	1,2,4-Trimethyl-1-Cyclohexene-4-Carboxaldehyde
10	9.8	13	37	35.1	Cinnamyl Formate
10	10.0	12	37	32.4	alpha-Terpineol
10	10.0	13	34	38.2	2,5-Dimethyl-5-Octanol
10	10.0	13	30	43.3	3,7-Dimethyl-1-Octanol
10	10.2	13	38	34.2	2,4-Decadienal
10	10.3	10	40	25.0	Verbenone
10	10.4	10	36	27.8	4-(3-Cyclohexen-1-yl)-3-Buten-2-one
10	10.5	14	30	46.7	Decahydronaphthalene
10	10.6	10	36	27.8	2,4,5-Trimethylbenzoic Acid
10	10.6	11	29	37.9	1-Decyne
10	10.8	8	34	23.5	7,8-Dihydrolinalool
10	10.8	11	25	44.0	2,2,5,5-Tetramethylhexene
10	11.0	9	29	31.0	p-Menthadien-1(7),8-ol-10
10	11.0	11	21	52.4	5-Decanone
10	11.2	8	41	19.5	2-(Butynyl) Cyclohexanone
10	11.3	11	24	45.8	2,7-Dimethyl Octanol
10	11.5	9	31	29.0	p-Menthen-8-ol-10
10	11.5	11	26	42.3	Spiro(4,5) Decane
10	11.5	12	25	48.0	1-Decene
10	11.7	14	30	46.7	2-Decyne
10	11.8	9	41	22.0	Carveol
10	11.9	8	31	25.8	Linalool
10	12.0	11	19	57.9	Pinane
10	12.1	6	54	11.1	3,6-Dimethyl-1-Thiaindene
10	12.3	12	30	40.0	Alpha-Fanchene
10	12.5	7	37	18.9	Anabasine
10	12.8	5	35	14.3	3,7-Dimethyl-2,6-Octadien-1-ol
10	12.8	8	33	24.2	Camphene
10	12.8	10	29	34.5	i-Menthol
10	12.9	9	35	25.7	Neoisothujyl Alcohol
10	13.0	6	31	19.4	Citronellal
10	13.2	9	29	31.0	Myrtenal
10	13.2	11	20	55.0	2-Propylheptanol
10	13.3	9	30	30.0	2-sec-Butylcyclohexanol
10	13.4	9	30	30.0	1,8-Cineole
10	13.5	11	27	40.7	Cyclodecanone
10	13.6	9	22	40.9	Cyclopentylcyclopentane
10	13.7	8	24	33.3	4-Cyclohexyl-2-Butanol
10	13.9	9	27	33.3	Menthol
10	13.9	9	24	37.5	5-Decyne
10	13.9	9	19	47.4	Di-i-Amylene
10	14.0	7	34	20.6	3-Allysalicylaldehyde
10	14.0	9	20	45.0	sec-Butylcyclohexane
10	14.2	9	23	39.1	6-Ethyl-3-Octanol
10	14.2	9	22	40.9	2,2-Dimethyl Octanol
10	14.5	6	30	20.0	Cumicaldehyde
10	14.7	1	13	7.7	Citronellol
10	14.7	10	39	25.6	i-Pulegol
10	14.7	10	10	100.0	Caran-2-ol
10	14.8	10	23	43.5	4,5-Dimethyl-4-Octanol
10	14.9	11	26	42.3	3-Decyne
10	15.1	6	21	28.6	4-Ethyl-1-Octyn-3-ol
10	15.2	9	30	30.0	Adamantane
10	15.3	9	19	47.4	2-Methyl-3-Nonene
10	15.4	9	20	45.0	8-Menthene
10	15.5	5	28	17.9	alpha-Tetranol
10	15.5	7	19	36.8	1-Octyl Vinyl Ether
10	15.5	9	20	45.0	Endo-i-Camphane
10	15.7	4	32	12.5	Cyclopentylcyclopentanol
10	15.8	8	20	40.0	4-Methyl-4-Nonanol
10	15.9	6	28	21.4	Dipentene
10	16.1	8	22	36.4	3,7-Dimethyl-3-Octanol
10	16.1	8	20	40.0	Exoiscamphane
10	16.2	7	15	46.7	1-Hexyl-1,3-Butadione
10	16.3	4	29	13.8	Umbellulone
10	16.3	6	19	31.6	Fenchone
10	16.3	10	10	100.0	Caran-3-ol
10	16.4	5	27	18.5	Neral
10	16.4	8	18	44.4	Fenchane

C	Σ_g	N25	N5	R	Compound
10	16.6	6	20	30.0	Ethyl 1-Phenylethyl Ether
10	16.9	7	20	35.0	1-Methyl-4-i-Propyl-3-Cyclohexene
10	16.9	9	22	40.9	4-Decyne
10	17.1	10	10	100.0	Caran-4-ol
10	17.2	2	32	6.3	i-Borneol
10	17.2	7	20	35.0	i-Butylcyclohexane
10	17.4	10	10	100.0	cis-Caranone-3
10	17.6	7	25	28.0	D-Limonene
10	17.7	3	23	13.0	p-Methylallylphenol
10	17.7	10	10	100.0	trans-Caranon-3
10	18.0	7	20	35.0	Camphor
10	18.1	7	20	35.0	Terpinolene
10	18.2	6	22	27.3	2,3-Dimethyl-5-i-Butylpyrizine
10	18.4	3	23	13.0	alpha-Tetralone
10	18.4	7	14	50.0	Methyl ar-Vinyl Ether
10	18.5	8	22	36.4	n-Butyl Cyclohexyl Amine
10	18.6	6	19	31.6	4-Ethyl-3-Octene
10	18.7	5	19	26.3	2-t-Butylcyclohexanol
10	18.8	6	16	37.5	3-Methylindan
10	18.9	6	22	27.3	1-Phenyl-2-Butene
10	18.9	6	14	42.9	2-Methyl-5-Ethylheptane
10	19.0	6	14	42.9	2,5-Dimethylmethylbenzoate
10	19.0	7	16	43.8	2,6-Dimethyloctane
10	19.1	6	20	30.0	Vinyl 2-Ethylhexyl Ether
10	19.2	7	12	58.3	2-Methyl-2,3-Dihydro-1,4-Benzopyran
10	19.3	2	21	9.5	Fenchyl Alcohol
10	19.3	3	23	13.0	Nerol
10	19.3	7	19	36.8	Benzyl Propionate
10	19.4	9	21	42.9	p-Menthen-1-ol
10	19.5	4	21	19.0	Terpinen-4-ol
10	19.5	6	18	33.3	4-t-Butylcyclohexanol
10	19.6	5	19	26.3	Myrcene
10	19.7	4	21	19.0	o-Diethylbenzene
10	19.8	3	22	13.6	2-Naphthalene Thiol
10	19.8	5	20	25.0	Nopinene
10	19.9	3	22	13.6	Methylallyl Phenyl Ether
10	19.9	7	14	50.0	2,7-Dimethyloctane
10	20.0	5	17	29.4	Alpha-Terpinene
10	20.0	5	12	41.7	4-Phenyl-3-Buten-2-one
10	20.0	10	10	100.0	Myrtenal
10	20.0	10	10	100.0	i-Menthone
10	20.3	4	22	18.2	Diethylcyclohexane
10	20.3	6	14	42.9	Di-n-Pentyl Ether
10	20.4	3	23	13.0	1,2,3,4-Tetrahydro-naphthalene
10	20.5	4	17	23.5	2,6-Dimethylstyrene
10	20.6	4	22	18.2	Carvomenthone
10	20.6	4	18	22.2	Trimethylbenzyl Alcohol
10	20.6	7	22	31.8	4-sec-Butylcyclohexanol
10	20.7	6	16	37.5	Allyl Benzyl Ether
10	20.9	2	19	10.5	1,7-Dimethylindole
10	21.0	3	20	15.0	5,7-Dimethylindole
10	21.0	5	21	23.8	3,8-Menthadiene
10	21.1	3	20	15.0	1,3-Diethylbenzene
10	21.1	7	16	43.8	2-Methylnonane
10	21.3	3	19	15.8	Lavandulol
10	21.4	4	18	22.2	Limonene
10	21.5	2	18	11.1	1-p-Menthen-9-al
10	21.5	4	19	21.1	a-Campholene Aldehyde
10	21.6	5	14	35.7	n-Decane
10	21.7	7	13	53.8	3,3,5-Trimethylheptane
10	21.8	4	19	21.1	(2-Methylpropenyl) Benzene
10	21.8	4	17	23.5	1-Methyl-4-i-Propyl-cyclohexane
10	21.9	5	19	26.3	2,4,6-Trimethylbenzoic Acid
10	22.0	3	17	17.6	o-Methallylphenol
10	22.0	4	18	22.2	o-Allyloxybenzaldehyde
10	22.1	3	21	14.3	6-Methyl Quinoline
10	22.1	3	18	16.7	Myrcene
10	22.2	2	20	10.0	Citral
10	22.3	4	16	25.0	n-Butylcyclohexane
10	22.4	3	20	15.0	2-Methylindan
10	22.5	3	21	14.3	5-Methyl-2-Furfurylfuran
10	22.5	4	18	22.2	4-Ethyl-2-Octene
10	22.5	6	13	46.2	3-Decanone
10	23.0	2	18	11.1	2-(1-Propenyl)-6-Methoxyphenol
10	23.0	3	20	15.0	p-Diethylbenzene
10	23.1	4	20	20.0	Methyl-1-Indene
10	23.2	6	15	40.0	3,6-Dimethyl-3-Octanol
10	23.3	3	14	21.4	2,5-Dimethylbenzo (B) Thiophene
10	23.3	5	15	33.3	Propyl Hexyl Keytone
10	23.4	4	18	22.2	i-Amyl Ether
10	23.4	4	17	23.5	4-n-Propyl-3-Heptene
10	23.7	3	15	20.0	4-t-Butylcyclohexanone
10	23.7	3	13	23.1	2,7-Dimethylbenzo (B) Thiophene
10	23.7	4	16	25.0	p-i-Propyl Benzoic Acid
10	23.9	3	19	15.8	Carvotanacetone
10	23.9	3	16	18.8	1-Methoxy-4-(1-Propenyl) Benzene
10	24.0	3	16	18.8	2,4,6-Trimethylbenzaldehyde
10	24.0	3	15	20.0	L-Phellandrene
10	24.0	4	18	22.2	1-Phenylpyrrole
10	24.1	3	15	20.0	Geranial
10	24.1	4	10	40.0	2,4-Dimethylacetophenone
10	24.2	3	14	21.4	Sabinol
10	24.5	6	12	50.0	Cuminyl Alcohol
10	24.6	3	16	18.8	m-Diethylbenzene
10	24.6	3	14	21.4	2,3-Dihydro-2-Methyl-benzofurancarboxaldehyde
10	24.8	1	20	5.0	Cyclofenchene
10	24.8	5	13	38.5	ar-Ethylphenethyl Alcohol
10	24.9	2	19	10.5	Thymol
10	25.0	4	12	33.3	3-Methylindene
10	25.5	5	15	33.3	4-Decanone
10	25.7	2	18	11.1	1,2,4,5-Tetramethylbenzene
10	25.7	3	16	18.8	3-Menthene
10	25.8	1	21	4.8	Nicotyrine
10	25.8	4	14	28.6	2,3-Dimethyloctane
10	26.1	3	16	18.8	3,5-Dimethylstyrene
10	26.2	3	15	20.0	o-Allyltoluene
10	26.2	7	10	70.0	Eucarvon
10	26.4	3	19	15.8	Geraniol
10	26.6	5	15	33.3	i-Propyl Benzoate
10	26.7	3	14	21.4	2,3-Dimethylindole
10	26.7	5	16	31.3	Allocimene
10	26.8	3	16	18.8	5-Methylindan
10	26.8	4	18	22.2	Carvone
10	26.8	5	14	35.7	p-t-Butylphenol
10	26.9	2	14	14.3	2,2-Prim-Bipyridyl
10	26.9	3	11	27.3	2,2-Dimethyl-4-Ethylhexane
10	27.0	3	13	23.1	4-N-Pentylpyridine
10	27.1	2	15	13.3	4-Methylindan
10	27.1	5	17	29.4	Gamma-Terpinene
10	27.1	5	12	41.7	2,4-Dimethylmethylbenzoate
10	27.2	4	16	25.0	Thujene
10	27.2	4	16	25.0	1-Menthene
10	27.2	4	12	33.3	t-Butylcyclohexane
10	27.6	3	12	25.0	o-t-Butylphenol
10	27.9	2	14	14.3	1,4-Diacetylbenzene
10	28.2	3	15	20.0	2-Cyclopentyl-1-Cyclopentanone
10	28.5	2	12	16.7	t-Butylbenzene
10	28.6	4	12	33.3	2-Decanone
10	29.1	4	13	30.8	4-n-Propylheptane

C	Σ_g	N25	N5	R	Compound
10	29.1	4	11	36.4	1,4-Naphthoquinone
10	29.2	2	16	12.5	3-Carene
10	29.2	2	11	18.2	m-Ethylstyrene
10	29.2	5	12	41.7	Di-i-Amyl Amine
10	29.3	3	9	33.3	1-Chloronaphthalene
10	29.4	2	13	15.4	i-Eugenol
10	29.5	2	13	15.4	Menthofurane
10	29.5	2	11	18.2	1,3-Dimethylindole
10	29.6	2	11	18.2	3-Acetylindole
10	29.7	1	17	5.9	1-Methylindan
10	29.9	4	11	36.4	3,4-Dimethylstyrene
10	30.3	2	13	15.4	p-Allyloxybenzaldehyde
10	30.4	3	14	21.4	Bicyclodihydrodipentadiene
10	30.5	3	15	20.0	Piperitone
10	30.6	4	14	28.6	2-Methyl-3-Nonanone
10	30.8	4	14	28.6	Alpha-Phellandrene
10	30.9	2	14	14.3	1,2,3,5-Tetramethylbenzene
10	31.0	2	12	16.7	Nicotine
10	31.1	2	14	14.3	1,4-Dimethyl-2-Ethylbenzene
10	31.1	3	15	20.0	Beta-Pinene
10	31.4	1	17	5.9	Tricyclene
10	31.5	2	8	25.0	2,5-Dimethylindole
10	31.6	2	8	25.0	2,6-Dimethylindole
10	32.4	3	11	27.3	2-Chloronaphthalene
10	32.6	2	16	12.5	Alpha-Pinene
10	32.6	2	13	15.4	1,3-Dimethyl-5-Ethylbenzene
10	32.9	2	10	20.0	Carvacrol
10	32.9	2	8	25.0	1,3,3-Trimethyl-2-Norboranone
10	33.2	2	13	15.4	1,2-Dimethyl-3-Ethylbenzene
10	33.3	2	11	18.2	n-Butylbenzene
10	33.5	3	12	25.0	Divinyl Benzene
10	33.6	2	8	25.0	m-Ethylphenyl Acetate
10	33.9	1	13	7.7	1-(2-Phenethyl)Azridine
10	33.9	3	8	37.5	Methyl Cinnamate
10	34.1	3	10	30.0	2,2,4-Trimethylheptane
10	34.4	1	12	8.3	1,2-Dimethyl-4-Ethylbenzene
10	34.5	3	7	42.9	i-Butylbenzene
10	34.7	2	7	28.6	ar,ar-Diethylphenol
10	34.9	3	7	42.9	1-Methyl-4-i-Propenylbenzene
10	35.0	2	12	16.7	p-Ethylstyrene
10	35.1	1	13	7.7	1-Methyl-2-i-Propylbenzene
10	35.1	1	13	7.7	2-N-Pentylpyridine
10	35.6	2	8	25.0	p-i-Propylanisole
10	35.8	1	13	7.7	o-sec-Butylphenol
10	35.9	3	8	37.5	3,5-Dimethylmethylbenzoate
10	36.0	2	10	20.0	Ethyl Phenyl Acetate
10	36.3	2	11	18.2	1-Methyl-3-i-Propylbenzene
10	36.7	2	13	15.4	1,3-Dimethyl-2-Ethylbenzene
10	36.8	1	13	7.7	Azulene
10	36.8	1	9	11.1	p-Diacetylbenzene
10	37.2	3	9	33.3	p-Ethylacetophenone
10	37.7	2	10	20.0	1,3-Dimethyl-4-Ethylbenzene
10	37.8	2	13	15.4	1-Methyl-4-i-Propylbenzene
10	37.9	3	10	30.0	i-Piperitenone
10	38.3	1	9	11.1	2,6-Dimethyl-3-Butylpyrizine
10	38.4	1	9	11.1	2,5-Dimethyl-3-Butylpyrizine
10	39.1	1	9	11.1	1-Methyl-2-n-Propylbenzene
10	39.3	2	9	22.2	p-Cymene
10	39.6	2	7	28.6	3-Phenylfuran
10	40.5	2	8	25.0	o-Cymene
10	41.3	1	7	14.3	4-Phenyl-1-Butene
10	42.0	2	7	28.6	2-i-Propyl-5-Methylphenol
10	42.2	1	8	12.5	3A,4,7,7A-Tetrahydro-4,7-Methanoindene
10	42.3	1	9	11.1	sec-Butylbenzene
10	42.8	2	5	40.0	m-n-Propyltoluene
10	43.2	1	8	12.5	n-Decyl Amine
10	43.5	2	7	28.6	i-Safrole
10	43.7	1	8	12.5	Borneol
10	44.2	1	8	12.5	1-Methyl-2-n-Propylbenzene
10	44.3	2	6	33.3	n-Butyrophenone
10	44.4	1	8	12.5	1-Methyl-4-n-Propylbenzene
10	44.4	2	7	28.6	2-Vinylbenzofuran
10	45.0	1	10	10.0	p-sec-Butylphenol
10	45.2	2	5	40.0	2-Naphthol
10	45.4	1	7	14.3	n-(1-Methylpropyl) Phenol
10	46.2	2	5	40.0	i-Butyrophenone
10	46.7	7	7	100.0	p-Cymene
10	47.4	2	5	40.0	(ar-Vinylphenyl) Acetic Acid
10	48.4	1	10	10.0	Naphthalene
10	49.4	1	6	16.7	o-n-Propyltoluene
10	49.9	1	6	16.7	p-Methoxy Propiophenone
10	51.5	1	8	12.5	1-Decylamine
10	52.3	1	6	16.7	1-Fluoronaphthalene
10	53.2	1	5	20.0	2-Fluoronaphthalene
10	53.4	1	6	16.7	n-Butyl Phenyl Ether
10	54.9	1	7	14.3	t-Butyl Phenyl Ether
10	56.3	1	6	16.7	Thujone
10	57.5	1	8	12.5	Allyl Benzoate
10	59.1	1	3	33.3	Pulegone
10	71.4	1	1	100.0	Menthone
10	72.2	1	3	33.3	2-Menthene
10	86.5	3	12	25.0	Sabinene
10	86.9	1	1	100.0	Beta-Phellandrene
11	10.2	10	42	23.8	6-Methyl-1,2,3,4-Tetrahydronaphthalene
11	10.5	10	39	25.6	Cinnamyl Ethyl Ether
11	10.6	11	29	37.9	Spiro (5,5) Undecane
11	10.7	10	38	26.3	3,4-Dihydro-4-Methyl-1(2H)-Naphthalenone
11	11.5	12	24	50.0	1-Undecene
11	13.0	6	36	16.7	5,6-Dimethylindan-1-one
11	14.9	7	19	36.8	3-Methyl-4-Phenyl-3-Buten-2-one
11	15.0	3	31	9.7	4,7-Dimethylindan-1-one
11	15.7	7	21	33.3	5-Methyldecene
11	17.6	7	16	43.8	4-Methyldecane
11	17.9	3	27	11.1	5,7-Dimethylindan-1-one
11	18.4	6	17	35.3	5-Methyldecane
11	19.8	3	15	20.0	5,6,7-Trimethylindole
11	20.3	7	15	46.7	2-Cyclohexyl-2-Methylbutane
11	20.6	4	20	20.0	p-(1,1-Dimethylpropyl) Phenol
11	20.6	6	14	42.9	n-Undecane
11	21.7	2	15	13.3	4-i-Propylacetophenone
11	23.3	3	14	21.4	1,2,3-Trimethylindole
11	23.6	2	22	9.1	2-Methyl-1,2,3,4-Tetrahydronaphthalene
11	23.9	4	16	25.0	Propyl Benzyl Keytone
11	24.1	3	18	16.7	3,3-Dimethylindan-1-one
11	24.3	5	11	45.5	1-Phenyl-2-Methylbutane
11	25.2	4	13	30.8	Neopentylbenzene
11	25.3	2	18	11.1	i-Butyl Propionate
11	25.6	2	19	10.5	1,2-Dimethylindan
11	25.7	3	13	23.1	2-Methyldecane
11	26.0	3	16	18.8	6-t-Butyl-m-Cresol
11	26.2	2	20	10.0	1-Methyltetralin
11	26.5	2	16	12.5	1,2,3,4-Tetrahydro-5-Methylnaphthalene
11	26.8	3	11	27.3	ar,ar-Diethyltoluene
11	26.9	3	9	33.3	1-Methoxynaphthalene
11	27.6	2	14	14.3	5,6-Dimethylindan
11	28.3	2	13	15.4	1-Phenyl-3-Methylbutane
11	28.5	3	11	27.3	6-t-Butyl-o-Cresol
11	28.6	2	6	33.3	1-Methylnaphthalene
11	29.0	2	13	15.4	1-Ethylindan

C	Σ g	N25	N5	R	Compound
11	29.0	2	13	15.4	1-Methyl-3-t-Butylbenzene
11	29.1	2	14	14.3	4,6-Dimethylindan
11	29.7	2	14	14.3	4,7-Dimethylindan
11	29.8	2	8	25.0	2-Methylnaphthalene
11	30.6	2	14	14.3	1-Methyl-4-t-Butylbenzene
11	31.5	2	16	12.5	1,6-Dimethylindan
11	31.7	3	11	27.3	p-i-Propenylacetophenone
11	31.9	2	12	16.7	2,6-Dimethylquinoline
11	31.9	2	11	18.2	2-Phenyl-2-Methylbutane
11	31.9	3	11	27.3	n-Pentylbenzene
11	32.1	3	9	33.3	p-Ethylcumene
11	32.7	3	7	42.9	2,4,6-Trimethylacetophenone
11	32.9	2	11	18.2	3-Phenylpentane
11	33.0	2	10	20.0	Pentamethylbenzene
11	33.1	2	13	15.4	3,5-Dimethyl-1-i-Propylbenzene
11	33.4	1	14	7.1	1,4-Dimethyl-2-i-Propylbenzene
11	33.4	3	9	33.3	2-t-Butyl-m-Cresol
11	33.5	2	14	14.3	1,3-Dimethyl-5-i-Propylbenzene
11	34.2	1	16	6.3	2-N-Hexylpyridine
11	34.4	1	14	7.1	1,3-Dimethyl-4-i-Propylbenzene
11	36.1	2	7	28.6	1-Methylbutyl Benzene
11	36.5	1	9	11.1	N-Benzylpyrrole
11	36.7	2	7	28.6	2-Methoxynaphthalene
11	36.9	1	12	8.3	1,1-Dimethylindan
11	37.1	1	9	11.1	p-t-Butylanisole
11	38.1	3	7	42.9	n-Valerophenone
11	39.6	2	8	25.0	4-t-Butyl-o-Cresol
11	41.5	2	7	28.6	2,5-Dimethyl-1-i-Propylbenzene
11	42.7	1	7	14.3	2,4-Dimethyl-1-i-Propylbenzene
11	42.8	1	10	10.0	2-Phenyl-2-Methylbutane
11	44.0	2	8	25.0	ar-Ethyl-1,2,4-Trimethylbenzene
11	45.5	3	7	42.9	t-Butyltoluene
11	45.7	3	7	42.9	m-Ethylcumene
11	49.0	3	6	50.0	Ethyl Methylstyrene
12	14.2	8	30	26.7	3-Phenylcyclohexene
12	15.4	6	29	20.7	1-Phenylcyclohexene
12	16.6	3	29	10.3	1,2,4-Trimethyl-5-i-Propylbenzene
12	17.5	7	27	25.9	Cyclododecatriene
12	20.5	3	24	12.5	2,3-Dihydro-1,4-Dimethylnaphthalene
12	21.8	4	14	28.6	1-Phenyl-2-Ethylbutane
12	25.3	4	17	23.5	Acenaphthene
12	25.4	3	17	17.6	m-Di-i-Propylbenzene
12	25.6	2	18	11.1	1,3-Dimethyl-5-t-Butylbenzene
12	26.0	2	13	15.4	3-Phenyl-3-Methylpentane
12	28.1	2	15	13.3	1-i-Propyl-3-i-Propenylbenzene
12	28.5	2	17	11.8	p-Di-i-Propylbenzene
12	29.3	2	13	15.4	4,5,7-Trimethylindan
12	29.4	2	12	16.7	1-i-Propyl-4-i-Propenylbenzene
12	29.5	3	13	23.1	1,6-Dimethylnaphthalene
12	30.0	2	14	14.3	2,3-Dimethyl-3-Phenylbutane
12	30.9	2	12	16.7	1,4-Di-n-Propylbenzene
12	32.1	2	12	16.7	1-Phenyl-3-Methylpentane
12	32.6	3	13	23.1	2A,3,4,5-Tetrahydro-acenaphthene
12	34.6	2	10	20.0	p-t-Butylstyrene
12	34.7	1	11	9.1	1,1-Dimethyl Tetralin
12	34.8	1	11	9.1	1-Ethyl-(1,2,3,4-Tetrahydronaphthalene)
12	34.9	2	8	25.0	1,2-Dimethyl-3,4-Diethylbenzene
12	35.2	2	10	20.0	1-Ethylnaphthalene
12	35.7	1	13	7.7	1,3-Dimethyl-4-sec-Butylbenzene
12	35.7	2	8	25.0	Hexamethylbenzene
12	36.2	1	10	10.0	1,1,6-Trimethylindan
12	36.2	3	7	42.9	Triethylbenzene
12	36.6	1	9	11.1	1,4,7-Trimethylindan
12	36.8	1	12	8.3	1,1,5-Trimethylindan
12	37.3	1	10	10.0	1,1,4-Trimethylindan
12	37.5	1	8	12.5	1,5,7-Trimethylindan
12	38.3	1	10	10.0	1,2-Di-i-Propylbenzene
12	39.3	2	6	33.3	Biphenyl
12	39.8	1	7	14.3	ar-t-Butyl-ar-Ethylbenzene
12	40.1	1	9	11.1	1,1,3-Trimethylindan
12	40.9	1	8	12.5	3-Phenylhexane
12	43.2	2	8	25.0	4-Phenylcyclohexene
12	43.9	1	11	9.1	2-Phenylhexane
12	45.0	3	4	75.0	ar-i-Propenyl-1,2,4-Trimethylbenzene
12	56.0	2	6	33.3	2-Phenyl-2-Methylpentane
12	59.0	1	4	25.0	ar-i-Propyl-1,2,4-Trimethylbenzene
12	78.9	1	1	100.0	2,6-Dimethylnaphthalene