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Selective mass spectrometry by single-photon ionization from a molecular hydrogen laser source

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SELECTIVE MASS SPECTROMETRY BY SINGLE-PHOTON IONIZATION FROM A MOLECULAR HYDROGEN LASER SOURCE

by

Jeffrey William Finch

A Dissertation Submitted to the Faculty of the DEPARTMENT OF CHEMISTRY In Partial Fulfillment of the Requirements For the Degree of DOCTOR OF PHILOSOPHY In the Graduate College THE UNIVERSITY OF ARIZONA

1992
As members of the Final Examination Committee, we certify that we have read
the dissertation prepared by Jeffrey William Finch
entitled Selective Mass Spectrometry by Single-Photon Ionization
from a Molecular Hydrogen Laser Source

and recommend that it be accepted as fulfilling the dissertation requirement
for the Degree of Doctor of Philosophy.

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Final approval and acceptance of this dissertation is contingent upon the
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SIGNED: Jeffrey William Finch
DEDICATION

This dissertation is dedicated to my wife, Julie Ann Finch. Her constant love, patience, emotional and financial support were of paramount importance in the successful completion of this work.

"He who finds a wife finds a good thing, And obtains favor from the Lord" Proverbs 18:22, New American Standard Bible
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ABSTRACT

A molecular hydrogen laser, with an output of 7.8 eV photons in the vacuum ultraviolet, is evaluated as a selective source for photoionization mass spectrometry. Types of compounds ionized by the laser include a variety of amines, nitrogen heterocycles, drugs of abuse, pharmaceuticals, and polynuclear aromatic hydrocarbons (PAHs). The laser is coupled to a time-of-flight mass analyzer, which allows a spectrum to be recorded with each laser pulse. The laser is a "soft" ionization source and mass spectra of nearly all of the compounds studied yield single ion peaks due to the parent molecule with no fragments. This results in simplified mass spectra with a one-to-one correspondence of photoactive molecules with molecular ion peaks. Since the photoionization threshold of the laser is relatively low, selectivity of the photoactive species is high in the presence of a complex sample matrix. The performance of the laser source is improved with a few changes in the original design. In addition, the previous method of recording mass spectra with a photographic emulsion is replaced with a digital oscilloscope, which averages spectra over many laser pulses. As a result, a true assessment of the technique's sensitivity is finally achieved. The time-of-flight mass spectrometer is modified with a new microchannel plate ion detector and preamplifier. As a result, detection limits for PAHs improve by nearly three orders of magnitude, from the 100 ng range to the 100 pg range.

Selectivity of the laser photoionization source in complex mixture analysis is demonstrated with the ability to detect PAHs in a drinking water sample at concentrations below 100 parts-per-trillion, using a simple solid-phase extraction technique. Application of the technique for rapid screening of drugs of abuse in urine is demonstrated where solid-phase extraction columns are utilized for sample pretreatment.
Urine samples spiked with drugs such as cocaine, codeine, morphine, phencyclidine, and methadone, yield photoionization mass spectra consisting of parent molecular ions for the drugs with a few non-interfering ion signals from the matrix. The technique is evaluated and compared to other drug screening techniques such as enzyme-multiplied immunoassay.
CHAPTER 1
INTRODUCTION

Mass spectrometry remains one of the most powerful techniques for the identification and quantitation of trace components in complex mixtures. However, due to the nonselective nature of typical ion sources such as electron impact (EI) or chemical ionization (CI), a chromatographic separation is usually necessary to isolate the desired component from a sample matrix before it enters the ion source. Combining a chromatographic separation step in this manner with mass spectrometry provides the sensitivity and selectivity necessary for analyzing a large variety of components in complex sample matrices. An example is the acceptance of gas chromatography/mass spectrometry (GC/MS) by the Environmental Protection Agency for the analysis of consent decree pollutants in waste water.

Although GC/MS is widely used, less than 1 percent of the 9 million compounds from the Chemical Abstracts Registry will pass through a gas chromatographic column, since many of these compounds are either highly polar, thermally unstable or of high molecular weight. It is estimated that approximately 50 percent of the remaining compounds will pass through a liquid chromatograph, and the application of new liquid chromatographic (LC) interfaces has extended the range of compounds analyzed by mass spectrometry. Recognizing the inadequacies of the moving-belt LC interface, a variety of new interfaces have been developed and reviewed. The application of these LC/MS techniques to the analysis of drugs and metabolites in biological fluids has recently been reviewed in the literature. Bowers has discussed the operation of each interface including advantages and disadvantages as well as the potential of LC/MS in the drug analysis laboratory. A variety of the new LC/MS interfaces are based on ion evaporation of components in the
LC effluent. Ion evaporation is a process where ions are ejected directly into the gas phase from charged droplets. Through this process, species such as polar biomolecular compounds can be introduced into a mass spectrometer in the form of quasimolecular ions. For the IonSpray and Electrospray interfaces, ion evaporation is achieved at atmospheric pressure. Quasi-molecular singly and multiply charged ions can be formed from peptides and polynucleotides greater than 10 kilodaltons (kDa) in molecular weight. The Thermospray interface also relies on the ion evaporation process, but utilizes heated nebulization to produce the spray and is limited in cases where molecules are thermally unstable. Another relatively new LC interface is the particle beam separator, where the effluent is nebulized, passed into a desolvation chamber, and directed through a momentum separator of two differentially pumped vacuum chambers. This produces a beam of desolvated particles which are believed to form ions from collisions with a surface in the ion source. This interface is capable of producing either electronic or chemical ionization spectra which can be compared with spectra in the library of the National Bureau of Standards.

Although LC/MS is now widely used in such areas as drug analysis, the techniques still suffer from disadvantages compared to GC/MS including lower sensitivity (limits of detection in the 5-100 ng range), high initial equipment costs, and additional time required to optimize chromatographic and interface conditions (up to several hours)\textsuperscript{5,6}. For complex environmental and biological samples, liquid and gas chromatographic separations usually require sample pretreatment to eliminate many of the matrix constituents which will absorb onto the column or bind to the molecule of interest. In the case of GC analysis for species such as drugs, derivatization of the analyte is often necessary to achieve separation, and this usually requires a more
extensive sample cleanup step. Finally, the time required for the chromatographic separation in GC or LC limits the speed of the analysis as well as the number of samples which can be analyzed on a routine basis.

In order to facilitate speed and convenience for complex mixture analysis, many analytical techniques have been developed with the goal of reducing the sample pretreatment required, without the need to pass the sample through a liquid or gas chromatograph. One unique example is fluorescence line narrowing, where freezing a fluorophore in a cryogenic aliphatic matrix results in narrowing its excitation and emission bands down to "quasi-lines" producing highly resolved fluorescence spectra. A tunable dye laser source can then be used to selectively excite one fluorophore in the presence of many others. Wehry and coworkers demonstrated the selectivity of the technique where benzo[a]pyrene and other polynuclear aromatic hydrocarbons were analyzed in a solid solvent-refined coal sample without any prior fractionation. One glaring disadvantage of the technique is the time required to completely deposit the sample in the cryogenic matrix, which is typically 2 hours.

Tandem mass spectrometry (MS/MS) is another example where techniques have been designed with the specific goal of reducing sample pretreatment and the need for lengthy chromatographic procedures. Two excellent fundamental reviews of MS/MS have been recently published. In general, this approach involves the combination of two or more mass analyzers, where the first mass analyzer (MS1) is utilized to select a desired molecular mass and pass it on to a cell filled with a neutral collision gas. The subsequent mass analyzer (MS2) is scanned to produce the spectrum of daughter ions produced from collisionally-activated dissociation (CAD) of the parent ion passed by the first analyzer. Scanning MS1 is analogous to separating components on a GC or LC column. The advent of direct mixture analysis by MS/MS was pioneered
in the laboratories of McLafferty\textsuperscript{10} and Cooks\textsuperscript{11,12} using the now commonly known reverse-geometry double-focusing mass spectrometer. MS/MS has been more widely used since the introduction of the triple quadrupole instrument by Yost and Enke in 1978\textsuperscript{13}. In this design, the first and third quadrupole mass filters (Q1 and Q3) function in a similar manner as MS1 and MS2 described above. The second quadrupole is operated in the Rf-only mode and acts as the collision cell, providing containment and focusing of fragment ions scattered by the collision process. Hunt et al. utilized a tandem quadrupole spectrometer for the direct analysis of p-nitrophenol and 2,4-dinitrophenol spiked in industrial sludge samples\textsuperscript{14}. Samples containing $\approx 10$ ng of each were freeze-dried and introduced into the ion source with a direct insertion sample probe (DISP) followed by negative OH chemical ionization. The $(M - 1)^-\text{ions}$ 138 and 183 were separated alternatively in Q1. A substantial number of ions were also generated by the sample matrix at these two masses, however Q3 was monitored for the $(M - H - NO)^-$ and $(M - H - NO_2)^-$ ions produced by CAD and high selectivity for the nitrophenols was achieved with a LOD estimated at 10 ppb. In addition, dioctyl phthalate was analyzed in sludge spiked at 100 ppb, where m/z 167 and 149 daughter ions were monitored from CAD of parent $(M + 1)^+$ ions produced from positive CI with isobutane. Estimated time of analysis was 10-15 minutes per sample. While this technique proved successful in reducing analysis time, there is much debate on how effective direct MS/MS analysis is for environmental samples versus GC/MS, GC/MS/MS, or LC/MS/MS. Bursey and Hass reported that their efforts analyzing crude samples with a DISP and high resolution tandem instrument failed, which was rationalized as a result of source de-tuning which takes place when large amounts of matrix material are introduced into the mass spectrometer\textsuperscript{15}. Furthermore, Bursey and Hass do not recommend the routine introduction of crude extracts into the ion source of a mass
spectrometer.

Analysis of drugs in biological fluids has prompted similar debate about direct MS/MS techniques. Yost and Brotherton demonstrated the ability to screen a wide variety of drugs in blood serum using a triple quadrupole mass spectrometer operated in the selected reaction monitoring (SRM) mode\textsuperscript{16}. In this mode, only the most intense daughter ion from each parent is monitored with Q3. Samples were either introduced directly or pretreated with a simple extraction. However, the technique was successful only if a relatively high concentration of drug was present in the sample, for example, detection limits for morphine in whole blood serum and extracted blood serum were 90 ppm and 75 ppm respectively. Detection limits were generally 2 to 40 times higher in serum samples analyzed directly than in chloroform solutions containing pure drugs. This was attributed to protein binding of the drugs and the high background generated by thermal decomposition of the serum matrix. Using an extraction procedure made it possible to screen a larger number of samples before servicing the instrument. However, for routine screening of 100 samples/day, the instrument still had to be disassembled once a week to clean the ion source and once a month to clean the first quadrupole. Phillips et al. attempted similar research on developing a technique for direct MS/MS analysis of whole blood samples spiked with morphine\textsuperscript{17}. However, direct probe analysis of blood samples spiked with 100 ppb of the drug gave poor signal to noise ratios, even when multiple daughter ions were monitored in Q3. Peaks from the matrix were observed at every mass and due to this high background interference, the direct analysis approach was abandoned. Instead, a simple extraction and derivatization procedure was employed, followed by separation on a short 5 m capillary column. By trading off increased sample pretreatment and analysis time, advantages of high sensitivity (1 ppb) and reduced instrument maintenance were realized.
Although the capillary column and glass injector insert had to be frequently replaced, the ion source only needed to be cleaned every month.

Even if samples can be directly analyzed by MS/MS techniques, there are still other disadvantages to consider. Although many tandem mass spectrometers are now commercially available, these instruments are very expensive when compared to the cost of a benchtop GC/MS. In addition, as demonstrated in the previous paragraph, the instrument requires more maintenance, particularly if used on a routine basis for the analysis of crude samples. One final disadvantage of direct MS/MS techniques is the fact that, for the analysis of multiple components in a sample, the two mass analyzers must be scanned in order to monitor each fragment or neutral loss reaction for a particular component. This limits the number of reaction pathways as well as the number of species which can be analyzed for a single sample run, since complete sample volatilization will occur within approximately a minute after heat is applied to the probe. Therefore it would be necessary to reanalyze the sample, possibly several times, for complete characterization.

In this chapter, two examples of direct analysis without a chromatographic step have been presented along with advantages and disadvantages of the particular approach. In the example of direct MS/MS analysis of complex mixtures, a mass selective separation is required to detect the desired components, since an abundance of ions from the matrix components will be produced in conventional EI or CI sources. An alternative approach is to utilize a more selective ionization source, where the species of interest could be ionized in the presence of a complex sample matrix. The ability to identify the desired components in a mixture is further enhanced when ionization is "soft", meaning that predominantly parent molecular ions are produced with limited fragmentation, yielding a simplified mass spectrum. This
is a distinct advantage noted for ion production in the ion evaporation LC/MS interfaces mentioned earlier.

As demonstrated in the example of fluorescence line narrowing mentioned earlier, photons of a particular energy are used to excite fluorophores in a complex matrix. In a similar fashion, a source of high energy photons can be utilized for soft, selective ionization of molecules in the gas phase for mass spectrometry. In photoionization MS, all molecules with ionization potentials at or below the threshold photon energy form ions and are directed into the mass analyzer, while other components are pumped away as neutrals. One unique source for "soft" photoionization is the molecular hydrogen laser which outputs 7.8 eV photons in the vacuum ultraviolet. In light of the advantages unique to photoionization, the principal goal of this research project is to evaluate the H$_2$ laser source for analytical mass spectrometry. Particular emphasis is placed on the ability to analyze trace levels of photoactive species in complex sample matrices, with minimal sample pretreatment. In evaluating the hydrogen laser source, it is important to discuss and compare other "soft" ionization sources commonly utilized in mass spectrometry. The next chapter will focus on these sources with particular emphasis given to photoionization sources and discussion of mechanisms in photoion formation.
CHAPTER 2

SOFT IONIZATION SOURCES AND PHOTOIONIZATION

Soft Electron Impact Ionization

While 70 eV electron impact ionization continues to be the most widely used mode of ionization in mass spectrometry, it is nonselective and generates extensive fragmentation. Since the ionization potentials of most organic compounds are in the range of 7-14 eV, one approach to reducing fragmentation and controlling selectivity is to lower the accelerating potential of the electron beam. Aczel and Hsu have utilized this approach where 12 eV EI was employed to simplify mass spectra of fossil fuel samples, limiting ionization to olefinic, aromatic, and polar components. However, efficiencies of 70 eV EI are estimated to be on the order of $10^{-3}$, and reduction of EI potential to the 10 eV range results in a significant decrease in efficiency. Furthermore, while low EI sources usually enhance molecular ion abundance, a large degree of fragmentation will still be observed in the mass spectrum.

Chemical Ionization

The technique of chemical ionization was first introduced by Munson and Field in 1966, where methane was used as the reactant gas. Chemical ionization is generally accomplished via ion-molecule charge transfer reactions occurring between reactant gas ions and gas phase sample molecules. The reactant ion is produced through a series of reactions following preionization (usually EI) of the reagent gas. Positive and negative ion production for mass spectrometry can proceed by a wide variety of ion-molecule reactions available with different reactant gases, as reviewed by Harrison. In CI ion-molecule reactions proceed at relatively high pressure (approx. a few torr) and without large transfers of energy. Therefore, little internal energy is
deposited into the ionized species, which results in predominant molecular ion production with less fragmentation than in the case of EI. For mixtures of sample molecules, selectivity can be achieved by exploiting differences in reactivity. For example, negative ion CI with N$_2$O reagent gas can be used to distinguish PAH isomer pairs such as benzo[e]pyrene and benzo[a]pyrene, due to differences in their mass spectra. Another example of selectivity is the use of ammonia CI for the analysis of amines in the presence of a hydrocarbon matrix. The NH$_4^+$ reactant ion will transfer a proton to the amines but will not react with hydrocarbons. The degree of fragmentation of the amines will be dependent on the exothermicity of the proton transfer reaction. For direct analysis of complex mixtures, chemical ionization still generally lacks the selectivity required to eliminate a chromatographic separation. For example, in the case of basic drugs in a simple urine extract, ammonia CI would not only transfer a proton to the drugs, but also to a considerable amount of the matrix constituents such as amino acids from proteins. In addition, reaction conditions in CI including temperature, pressure, and purity of the reagent gas must be very carefully controlled to ensure reproducible ion signals.

Desorption Ionization Methods

Soft ionization can be achieved in a variety of techniques where molecular ions are desorbed from a solid or liquid matrix, with little excess energy imparted to the ionic species. Fast atom bombardment (FAB MS$^2$, secondary ion MS (SIMS$^2$), field desorption and field ionization MS (FDMS and FIMS$^2$), plasma desorption MS (PDMS$^2$) and laser desorption MS (LDMS$^2$) have demonstrated the capability to produce intact molecular ions for a variety of compounds such as polymers and biomolecules. A significant aspect of these techniques is the ability to obtain accurate molecular weight information for large, nonvolatile species. One of the most exciting recent developments in mass spectrometry is the
introduction of UV and IR matrix-assisted laser desorption for very large biomolecules from the laboratories of Hillenkamp et al. and Chait et al. The key to matrix-assisted laser desorption is mixing the sample with a high molar excess of an solid or liquid organic matrix having a strong absorption at the laser wavelength. Proteins, polynucleotides, and carbohydrate molecules with molecular weights as high as 300,000 have been successfully analyzed with sensitivities in the femtomol range and mass errors on the order of $10^{-3}$-$10^{-4}$.

While these desorption techniques are invaluable for obtaining molecular weight information, the nature of sample introduction gives rise to disadvantages for routine analysis, where samples must be mixed in a liquid or solid matrix and placed on a solid substrate. Desorption techniques suffer from irreproducible ion signals which are critically dependent on sample/matrix concentration. In addition, ion signals from the matrix can interfere with analyte signals, particularly in the low mass range of 1-1000.

Photoionization

Mechanisms of Ion Formation In Photoionization

Before discussing photoionization sources for analytical mass spectrometry, it is important to examine mechanisms of photoabsorption and photoion formation in the gas phase. For a more detailed description of photoionization phenomenon, refer to Berkowitz and Eland.

Processes For Photon Energies Below The First Ionization Potential

Upon absorption of incident radiation less energetic than the first ionization potential (IP1), the molecular system is promoted to discrete states. Low-lying states are termed valence states while higher energy states are described by the Rydberg formula:
where $E_n$ is the energy of the nth level, $R$ is the Rydberg constant ($109,737 \text{ cm}^{-1}$), and $\delta$ the quantum defect. The quantum defect accounts for the fact that molecules are not point charges but have finite structure. Existence of an infinite number of electronic energy levels below the ionization potential of a molecule is a manifestation of the Rydberg equation.

When a molecule absorbs a photon of energy below $IP_1$, the system can either be elevated to a discrete excited state

$$AB + hv \rightarrow (AB)^*$$

or dissociated into separate species:

$$AB + hv \rightarrow A + B$$

$$AB + hv \rightarrow A^+ + B^-$$

Equation 3 is termed direct dissociation while Equation 4 is termed direct ion-pair formation. Therefore, ionization of the molecular species is possible where the photon energy ($hv$) is below $IP_1$, provided that the following requirement is met:

$$IP^A - EA^B + D_o^{AB} < hv$$

where $IP$, $EA$ and $D_o$ are the ionization potential, electron affinity, and dissociation energy, respectively.

Molecules promoted to an excited state below $IP_1$ via process (2) can undergo reradiation:

$$AB^* \rightarrow AB + hv$$

predissociation into a neutral pair:
or predissociation resulting in ion-pair formation:

\[ AB^* \rightarrow A' + B^- \]  \hspace{1cm} (8)

These predissociation processes occur due to the nature of the excited \( AB^* \) state, which is a "mixture" of two or more wave functions degenerate in energy. The excited molecule can therefore undergo a radiationless transition and predissociate, as illustrated in Figure 2.1a and b. For most molecules which form ion pairs, Equation 8 is the predominant mechanism over Equation 4. Ion-pair formation below IP1 is observed for halogens \( F_2, Br_2, I_2 \), halides HF, HCl, and simple alkyl halides such as \( CH_3Cl \) and \( CH_3Br \). This indicates that Equation 8 is most likely to arise only when \( E_{AB} \) is large (Equation 5) as is the case when \( B \) is a halogen atom.

**Processes For Photon Energies Exceeding The First Ionization Potential**

When molecules in the gas phase are irradiated with photons of sufficiently high energy (i.e. in the vacuum-ultraviolet range), a bound electron in the molecular system can be raised to the ionization continuum yielding direct photoionization (Figure 2.2):

\[ AB + h\nu \rightarrow AB^* + e^- \]  \hspace{1cm} (9)

The process demonstrated in Figure 2.2 is a Franck-Condon mediated event. According to the Franck-Condon principle, electronic transitions occur rapidly with respect to nuclear motions, so the molecular ion is formed in a vibrational state in which the positions and momenta of the nuclei are essentially the same as in the initial state. Therefore, photon-induced transitions occur vertically without a change in internuclear distance, and only transitions to certain states will be readily allowed. Assuming that electronic excitation of the resulting
Figure 2.1 Diagrams of photoionization processes which can occur below the first ionization potential for the molecule AB: (a) neutral pair formation, (b) ion pair formation.
Figure 2.2 Single-photon ionization.
positive ion is negligible, the kinetic energy of the ejected photoelectron, KE is described by:

\[ KE = h\nu - I_j - E_{\text{vib,rot}}^* \]  \hspace{1cm} (10)

where \( I_j \) is the binding energy of the electron in the \( j \) orbital and \( E_{\text{vib,rot}}^* \) is the vibrational and rotational energy excitation energy of \( AB^+ \). The minimum photon energy required to produce the molecular ion in its 0-0 electronic state is the ionization potential (IP) or threshold energy. Theoretically, if the photon energy is closely matched to this threshold, only parent molecular ions will be observed in a mass spectrometer because ions will be formed with little excess energy. This is the ideal case for soft photoionization. However, discrete superexcited states can be imbedded in the ionization continuum. These states can arise from the following mechanisms: two-electron excitation, inner-shell excitation, spin-orbit splitting, and vibrational excitation of Rydberg states. In reality, these electronic states must be within 1 eV above the ionization potential, since vibrational energy imparted to a molecule via photoabsorption is not much greater that this value. Upon promotion to these superexcited states, the molecular system can undergo mechanisms such as predissociation into a neutral pair (Figure 2.3a):

\[ AB + h\nu \rightarrow AB^{**} \rightarrow A + B \]  \hspace{1cm} (11)

In addition, nonradiative decay from a superexcited level into the ionization continuum results in the mechanism called autoionization (Figure 2.3b):

\[ AB + h\nu \rightarrow AB^{**} \rightarrow AB^+ + e^- \]  \hspace{1cm} (12)

While fragmentation of small molecules can be interpreted in terms of classical mechanisms based on Franck-Condon factors, potential energy curves and asymptotic limits, larger molecules represent more complex
Figure 2.3 Processes which can occur upon excitation of a molecule $AB^0$, to superexcited state $AB^*$: (a) predissociation into a neutral pair, (b) autoionization.
systems which require a separate approach. This approach is termed quasi-equilibrium theory (QET). Since large molecules will contain a higher density of states, non-radiative decay of excess energy imparted to the molecular ion will occur very rapidly due to the availability of these state. According to QET, fragmentation can be viewed as a two stage process. Upon formation of the molecular ion, any excess electronic and vibrational energy is rapidly "randomized" or redistributed into vibrational phase space of the ground electronic state of the molecular ion. The phase space represents all vibrational conformations having this same energy and each conformation is accessible during ion formation. The molecular ion then undergoes dissociation because some of the conformations are favorably disposed toward bond cleavage. Each of these conformations act as a "sink" to dissipate the excess energy, leading to a set of competing fragmentation channels for unimolecular dissociation.

Photoionization Sources For Mass Spectrometry

Laser Multiphoton Ionization

Multiphoton ionization can occur when molecules are promoted into the ionization continuum by absorption of two or more photons from an intense UV or visible light source. The advent of high-power tunable visible and UV laser sources has made this a viable approach for analytical mass spectrometry. When a dye laser pumped by a Nd-YAG laser is tuned to a wavelength of UV light which is resonant to a real intermediate electronic state of a molecule, the ionization cross-section is greatly enhanced. This approach, illustrated in Figure 2.4a, is termed resonance-enhanced multiphoton ionization. Since the resonant intermediate state is relatively long-lived \(10^4\) sec, the molecule has a high probability of absorbing an additional photon before relaxing, and very efficient ionization is possible at intermediate laser powers \((10^6-10^7 \text{ watts/cm}^2\text{ per laser pulse})\). Smalley et al. have reported
Figure 2.4 Photoionization strategies for mass spectrometry.
ionization efficiencies approaching 100% for REMPI of transition metal carbonyls and aniline. REMPI in mass spectrometry has been reviewed by Lubman. Selectivity for ionization is further enhanced by "freezing out" many of the rotational and vibrational modes available to the photoactive molecule prior to photoionization. This is achieved by seeding the compound in a supersonic expansion of a gas such as He or N₂, which results in collapsing the broad-banded absorption spectra to several sharp lines. Lubman and Kronick demonstrated the ability to obtain soft ionization (REMPI at 266 nm) for species such as polynuclear aromatic hydrocarbons introduced as effuse molecular beams into the ion source of a time-of-flight instrument. Fragmentation patterns of the PAHs were critically dependent on laser power. For a mixture of aniline, naphthalene, 2-methylnaphthalene, and 2,4-dimethylnaphthalene introduced through a pulsed supersonic expansion valve, each component could be selectively ionized by tuning the dye laser to a narrow absorption line unique to a particular molecule. Lubman et al. applied this same approach to discriminate among four isomers of dichlorotoluene. Dobson et al. utilized REMPI for GC detection with a TOF mass spectrometer for the analysis of PAHs. Using a compromised excitation wavelength of 285 nm (1 millijoule pulse energy), detection limits in the low picogram range were possible.

In addition to REMPI, molecules can be ionized by promoting an electron into the ionization continuum through photoabsorption into one or more virtual states, as illustrated in Figure 2.4b and c. Since these states are very short-lived ($10^{-15}$ sec), absorption of two or more photons must occur almost instantaneously before the molecule relaxes. Thus, nonresonant multiphoton ionization requires very high photon fluxes on the order of $10^{29}$ photons cm$^{-2}$ sec$^{-1}$ ($10^{10}$ watts/cm$^2$). Sources capable of producing nonresonant two-photon ionization include the ArF excimer laser (193 nm, 6.42 eV) and the KrF excimer laser (249 nm,
5.0 eV). While these sources are capable of producing molecular ions with little fragmentation, efficiencies are typically several orders of magnitude below those possible with resonant MPI techniques. Another disadvantage is that, due to the high photon flux involved, extensive fragmentation can also result from absorption of additional photons by the molecular ion or neutral photofragments. As a result, nonresonant MPI mass spectra resemble those of low-energy electron impact as demonstrated by Decorpo et al.

In summary, while laser MPI sources are a viable approach to soft ionization, there are other factors to consider. For REMPI, the ability to obtain soft ionization will be dependent on the laser power as well as the wavelength used. Therefore, to analyze a range of compounds in a complex mixture, it will be necessary to change the wavelength and the power for each component. For tunable dye lasers, the ability to match wavelength energy to ionization potentials is limited by the narrow range of tunable frequencies available at each principle harmonic. As a consequence, when molecules with lower IP's are ionized universally with the 266 nm harmonic ($E_{\text{int}} = 9.3$ eV), fragmentation is accompanied by molecular ion formation, even at low laser powers. This is due to excess energy imparted to the molecule upon ionization, which leads to dissociation of the molecular ion. Lubman et al. reported fragmentation for tricyclic antidepressants such as imipramine introduced as expansions from supercritical water or methanol with REMPI at 266 nm and 1 mJ pulse energy. The necessity to change the incident wavelength is even more critical for selectivity when compounds are supercooled with a pulsed expansion nozzle. While this approach for sample introduction improves selectivity, the pulsed expansion nozzle is a very complex system and is subject to problems such as clogging.

**Sources for Single-Photon Ionization**

Since the ionization potentials of most molecules lie in the range
of 7-16 eV, single-photon ionization (Figure 2.4d) requires high energy photons in the vacuum ultraviolet (VUV) spectrum, corresponding to a wavelength range of 1250-775 angstroms. Metal vapor and noble gas discharge lamps coupled with VUV optics are capable of producing photon energies in excess of 10 eV. An excellent review of these sources and their application in VUV spectroscopy has been published by Samson46.

The first application of photoionization in mass spectrometry was reported in 1929 by Ditchburn and Arnot, for mass analysis of K+ ions from potassium vapor irradiated with an iron arch source47. In 1932, Terenin and Popov demonstrated the existence of an ion pairing mechanism in the mass analysis of thallium halides irradiated with resonance lines of Cd, Zn, or Al arc sources isolated with a simple quartz prism monochromator48. In the 1950's, photoionization mass spectra for simple organic compounds using gas discharge lamps were reported from a number of researchers49,50. Morrison utilized a discharge lamp/monochromator source for measurement of ionization and appearance potentials for simple molecules49. In this approach, the photon beam energy resolution (approx. 0.5 eV) allowed a more accurate measurement than was possible for conventional EI sources. Applications of single-photon ionization in mass spectrometry with noncoherent sources such as gas discharge lamps has been the subject of a review by Reid52.

While noncoherent sources have proven to be valuable in mass spectrometry for areas such as the study of ionization mechanisms, application of these light sources in analytical mass spectrometry has been limited. This is primarily due to the relatively low intensity of VUV photons, which is typically on the order of 10⁷-10⁸ photons/sec for condensed spark discharge lamps of Xe, Kr, Ar, Ne, He, or H₂, which are considered to have the highest intensity46. In addition, due to the noncoherent nature of these sources, the intensity decreases as 1/(distance)². Therefore, in a vacuum environment, the lamp must be as
close to the ion source as possible. In contrast, laser sources can be conveniently located at a distance from the ion source, without a significant loss in intensity.

Single-photon ionization with a coherent 10.5 eV source for mass spectral analysis has been recently reported by Van Bramer and Johnson\textsuperscript{53}. The radiation was produced by frequency tripling the third harmonic of an Nd:YAG laser (355 nm) in a cell containing a mixture of Xe and Ar. Molecules such as n-alkanes, alkenes, ketones, carboxylic acids, and ethers gave predominant molecular ions with little fragmentation. Aldehydes and amines gave significant molecular ion signals but extensive fragmentation was observed, while branched alkanes, dienes, alcohols, and esters gave little or no molecular ion signal. However, the laser cell is a complex system, requiring research purity (99.999\%) gases and meticulous pretreatment of the cell to eliminate the presence of any contaminants. When adding each gas, the pressures of the two gases must be accurately monitored, due to the narrow pressure range over which the Xe/Ar mixture is correctly phase matched\textsuperscript{44}. VUV efficiency drops off after several days and the cell must then be evacuated, baked out, and refilled which results in considerable downtime for routine analysis.

Another coherent source of VUV photons is the molecular hydrogen laser, which is the foundation of the research described in this dissertation. The device outputs 7.8 eV photons over a series of lines arising from Lyman transitions at around 160 nm. Lasing action in H\textsubscript{2} is achieved with a Blumlein discharge apparatus which is relatively simple in design, requires low maintenance, and is easy to operate. Types of compounds ionized by the laser include a variety of amines, nitrogen heterocycles, PAHs, drugs of abuse, and pharmaceuticals. For nearly all of the compounds studied, only the parent molecular ion is produced.

The next chapter will focus on the instrumental design of the H\textsubscript{2}
laser, beginning with a literature review of the laser that includes applications of this unique source to mass spectrometry.
CHAPTER 3
THE MOLECULAR HYDROGEN LASER SOURCE

Background And Applications To Mass Spectrometry

The feasibility of obtaining lasing action in the VUV by electron impact excitation of \( \text{H}_2 \) was first suggested by Bazhulin et al. in 1965\(^8\). Based on a rate equation analysis, Ali and Kolb predicted that lasing action for Werner bands of \( \text{H}_2 \) between 102.5-123.9 nm could be achieved\(^8\). In a high-current discharge with a fast risetime of a few nanoseconds, electron impact excitations of electrons to vibrational levels of the \( \text{C}^3\Pi_u \) electronic state would result in a population inversion with respect to the empty vibrational levels of the \( \text{X}^3\Sigma^+ \) state. Assuming a capacitance voltage of 150 kV and a discharge channel pressure of 10 torr, peak laser power densities were calculated to be in the kW/cm\(^3\) range for the strongest lines. To prove these predictions for hydrogen, Wayant et al.\(^7\) constructed a parallel-plate Blumlein system in 1970. This system was based on a design published in 1967 by Shipman\(^8\), which was used to produce lasing action in \( \text{N}_2 \) and \( \text{Ne} \). While Wayant and coworkers were unable to observe any Werner lines, intense lines in the VUV range of 156.7-161.3 nm were observed for lasing action from Lyman bands (\( \text{B}^4\Pi_u^+ \rightarrow \text{X}^3\Sigma^+ \)). The Blumlein device used in this study, which was capable of excitation currents of hundreds of kiloamps with voltages of 100 kV, consisted of a discharge channel acting as a resistive load between two top metal plates which are separated from a bottom plate by a layer of mylar dielectric. With one top plate at high voltage and the bottom plate at ground, a series of dielectric solid switches connecting these two plates were fired sequentially to produce an excitation wave transverse to the channel length which traveled at the speed of light. Intensity measured for the 160.0 nm line at the end of the channel toward which the wave traveled was ten times higher than the intensity.
measured at the opposite end. Wayant and coworkers cited this amplification effect as proof of lasing action. At about the same time period, Hodgson also reported lasing action from the Lyman bands of H₂ with a similar Blumlein device which utilized a single solid dielectric switch, located at the center of one of the top plates⁹. By calibrating fluorescence intensity response of a sodium salicylate screen for lasing action of N₂, the total peak energy per pulse for H₂ was estimated at 3 µJ, which corresponded to a power of 1.5 kW. In addition, it was discovered that power output was critically dependent on H₂ pressure, with a broad maximum near 60 torr.

In 1972, Hodgson and Dreyfus observed lasing action for H₂ (Lyman bands only) with a device using electron excitation from a beam of electrons directed down a steel tube (175 cm long, 1.9 cm i.d.) filled with 50 torr of hydrogen⁹. In this configuration, a 3 nsec pulse of 400 keV electrons from a field emission diode were confined by an axial 2-10 kG magnetic field from a pulsed solenoid surrounding the tube. This device was later modified with a longer, narrower tube (2.3 m, 1 cm i.d.) and a higher e⁻ beam energy (5 X 10⁹ W), to produce the first report of lasing action for Werner bands in the 116.1-124.0 nm region⁶. Improved powers of 400 kW/cm were also reported for several of the Lyman bands. In 1974, Hodgson and Dreyfus modified this design further with a 4 gigawatt e⁻ beam and a tube which was cooled to liquid N₂ temperatures⁶. Lasing action in Werner bands down to 109.8 nm was observed. By lowering the temperature of the gas, the excitation cross section for the Werner and Lyman transitions should increase, resulting in a proportional increase in power. However, it was discovered that output energy from the strongest Werner lines increased by only an order of magnitude or less, while the Lyman bands showed only a moderate increase. This indicated that the laser was operating in the saturated gain region with respect to the stronger lines, particularly in the
Lyman band. Experimentally measured photon fluxes for Lyman bands were as high as $10^{13}$ photons/cm$^2$. One significant disadvantage of the electron tube design is the reported 50% pulse-to-pulse variation in laser energy.

Up until the mid 1970's, practical applications of the hydrogen laser to photochemistry and mass spectrometry were limited. Earlier Blumlein systems relied on solid-state dielectric switches which provided only single-shot operation (one shot every 2-20 min), while electron beam tube systems were very complex and suffered from disadvantages such as irreproducible pulse intensities. Noting the problems of earlier designs, Andreyev and researchers from the Institute of Spectroscopy at the USSR Academy of Sciences designed a hydrogen laser based on a Blumlein system which utilized a low-inductance spark gap switch. A repetition rate of 10 Hz was reported with a 1 nsec pulse duration and a 0.1 mW mean power for the cluster of Lyman lines around 161.0 nm. Photoionization current yields for methylaniline and dimethylaniline were measured with the device and it was predicted that the photon flux would be sufficient to detect $10^4$-$10^5$ molecules. The Soviet team also investigated the luminescence of NaCl and KBr crystals irradiated with the same H$_2$ laser and found that peak photointensity was ten orders of magnitude higher than that obtained with a capillary H$_2$ discharge lamp. In 1977, the same principle investigators demonstrated single-step photoionization of NO from lasing action of the 120.0 nm Werner line. Based on the photoionization current yield of NO, a power of 1 μW for the weak 120.0 Werner line was estimated for a duty cycle of 10 Hz. In addition, two-step photoionization was reported for NO$_2$ using a dye laser (2.7 eV)/H$_2$ laser (7.8 eV) scheme and for H$_2$CO using a N$_2$ (3.7 eV)/H$_2$ laser combination. The design in this study utilized a narrow discharge channel (0.03 cm X 2 cm X 30 cm) and a spark gap switch purged with N$_2$. Discharge voltages
of 40 kV were possible for repetition rates of up to 300 Hz.

For the Lyman transitions in the VUV, the upper laser level has an extremely short radiative lifetime of 0.8 nsec\(^6\), while the lower laser level is metastable. Therefore, it is critical that the discharge in the H\(_2\) laser has a rapid rise time (on the order of 1 nsec or less), so that molecules are excited to the upper laser level more quickly than they spontaneously reradiate and are then "trapped" in the lower level. Recognizing these facts, Goldsmith and Knyazev argued that there is no utility in designing lasers with long transmission lines or large Blumlein plates, since the useful duration of the discharge is limited to \(\approx 1\) nsec\(^6\). Goldsmith and Knyazev published a simple, compact (36 X 49 cm transmission line) design for the H\(_2\) laser in 1977, and measured pulse energy dependence on a variety of factors such as voltage, discharge channel height, H\(_2\) pressure, and spark gap pressure. An average peak pulse energy of 20 \(\mu\)J (40 kW), was reported for a 300 \(\mu\)m channel height filled with 45 torr H\(_2\) operating at 40 kV and a duty cycle of 10 Hz. In 1981, Kim et al. measured the speed of the traveling wave discharge in a novel slotted Blumlein transmission line operating on hydrogen\(^6\). Two fiber optic rods coupled to photomultiplier tubes were placed at varying distances along the discharge, and the time delay between the arrival of light at each point was measured. Based on these results, the determined speed of propagation was 2.52 \(\pm\) 1.8 m/sec.

For optimum intensity from the hydrogen laser source, it is critical that the discharge channel height is uniform along the entire channel distance. In 1985, Denton et al. published a novel technique to satisfy this criterion for discharge channel construction\(^6\). Two channel halves were formed from stainless-steel sheets (0.01" thick with 1 mm edge bent at 90\(^\circ\)) sealed in three pieces of glass with epoxy. Then the two halves were epoxied together between two tautly drawn piano wires supported by a frame. The piano wires, with a tolerance of 0.0002",
provided a uniform channel height and wire of different diameters could be used to construct channels of a desired height.

The first application of the H₂ laser source in mass spectrometry was reported by Potapov and coworkers in the Soviet Union in 1978. For one-step photoionization of dimethylaniline, ion current measured with the H₂ laser exceeded the ion current yield measured with a H₂ discharge lamp by five orders of magnitude. Coupling the output of the H₂ laser with a N₂ laser or a N₂ pumped dye laser into the ion source of a mass spectrometer made it possible to investigate the kinetics of two-step photoionization processes for benzaldehyde, benzophenone, nitrobenzene, p-nitrotoluene, and o-nitrotoluene.

In 1985, Huth and Denton reported on the utility of the H₂ laser source for analytical mass spectrometry. In this study, the laser was coupled to the ion source of a linear time-of-flight system. For compounds with ionization potentials below 7.8 eV, only the parent molecular ion was observed in the mass spectrum. The types of compounds ionized below 7.8 eV include a variety of secondary and tertiary amines, nitrogen heterocycles, and polynuclear aromatic hydrocarbons. For a mixture of diethylamine (IP = 8.0 eV) and triethylamine (IP = 7.5 eV), the mass spectrum contained only a parent molecular ion signal for triethylamine, which emphasizes selectivity of the laser source. In a second study, Huth and Denton demonstrated selectivity of H₂ laser photoionization for the direct analysis of simple extracts from complex matrices spiked with photoactive compounds. Beer, soy sauce, and coffee samples spiked with 50 ppb 4-methoxyaniline were made alkaline to pH 11, extracted in CH₂Cl₂, back-extracted into 1 M HCl, made alkaline once again and re-extracted into CH₂Cl₂. Residues of the extracts, introduced into the ion source with a direct insertion sample probe (DISP), gave mass spectra with a clear M⁺ signal for 4-methoxyaniline and only 4-8 peaks from the matrix. Alkaline extracts from urine and
serum samples spiked with three phenothiazine tranquilizers at the 100 ppb level gave similar results. One drawback of the technique was the photographic method of data acquisition (oscilloscope/camera system), which limited the ability to obtain quantitative information such as an estimation of detection limits.

**Instrumentation: The Molecular Hydrogen Laser Source**

Details of the basic design of the molecular hydrogen laser used in this study have been discussed previously by Babis[67]. This design is based on that of Knyazev and Goldsmith[67] which is a Blumlein system with a low-inductance spark gap switch.

**Blumlein Transmission Line and Discharge Channel**

A side view of laser design is illustrated in Figure 3.1. Dimensions of the inner discharge channel were 16" X 3/4" X .013" (330 μm) and details of the channel construction have been previously described[6]. The ends of the channel were epoxied into lucite blocks which contain 1/4" Swagelock (Solon, OH) fittings for the gas and vacuum lines. Each block has a 3/4" hole drilled in the end with an O-ring groove at the face. The channel was sealed with two flange assemblies which secure a 1" diameter 2 mm thick CaF window (Janos Optical Co., Townshend, VT) to each face of the channel. The two stainless-steel electrode sheets rest underneath the top Blumlein plates. In addition, a 70 μH inductor was attached between the two top plates to maintain continuity of the plates between pulses. All three plates were made from 1/8" thick sheets of aluminum. The bottom Blumlein plate is 30" X 17" with a curved edge running from the left bottom edge to a point 17" from the right top edge. This plate is wrapped with eight layers of 0.05" thick mylar dielectric (see Appendix B). One top plate was a rectangle of dimensions 17" X 11.5" while the plate containing the spark gap assembly is 17" X 14" with a curve running along the entire right hand side which matches the bottom plate. The laser assembly rests on a
Figure 3.1 Diagram of the hydrogen laser system, side view.
support frame of lucite planks which are attached inside a sheet metal box measuring 34" X 24" X 2". To compress the Blumlein assembly and seal the spark gap, five lucite planks are placed across the top plates and bolted to the frame with large plastic screws. Three plastic screws also secure the blocks of the discharge channel to the frame. A 34" X 24" sheet metal box, 7" deep, acts as a cover and is bolted to aluminum strips inside the shallow box with 6-32, 1/4" screws spaced ~3" apart. This serves to suppress Rf noise emitted from the laser. For addition Rf noise suppression, copper mesh is fastened over the hole where the high voltage cable comes into the laser box and around the large square holes where the discharge channel flanges emerge from the sides of the box.

The high voltage power supply, trigger generator, and gas controls for the laser were all housed in a 19" rack, 5.5' high and 30" deep. 220 V, 3 phase power and 110 V power are brought into the rack from two receptacles mounted on the ceiling panel, which also contains a 9.5" cooling fan.

Gas Supply

The gas handling system for the laser is illustrated in Figure 3.2. A Kinney Vacuum Co. (Boston, MA) Model KC-8 mechanical rough pump was used to draw a vacuum on one side of the discharge channel and the vacuum is regulated with a 1/4" leak valve (Robbins Aviation Co). The flow of hydrogen into the other side of the channel is controlled with another 1/4" leak valve and monitored with a 1/8" tube flowmeter (Lab Crest) placed in the gas line. A Wallace & Tiernan (Belleville, NJ) Model FA 141 differential pressure gauge was used to monitor the pressure of H₂ in the channel. The pressure gauge, flowmeter, and valves were mounted on a 12" X 19" panel inside the laser rack. On the panel, one valve is labeled "VACUUM" while the other is labeled "GAS INPUT". Lengths of rubber vacuum hose are used to link the panel
Figure 3.2 Gas handling system of the hydrogen laser: A-discharge channel; B,F-leak valves; C-flowmeter; D-differential pressure gauge; E-rough vacuum pump; H-psi pressure gauge; I-metering valve.
control lines to the hydrogen laser, rough pump, and H₂ gas cylinder. For the spark gap, pressure is controlled from the N₂ cylinder regulator, while the flow is controlled with a 1/4" Nupro (Willoughby, OH) Model S-SS4-A metering valve located at the end of the purge line. A 0-300 psi gauge (U.S. Gauge Co.) was placed between this valve and the spark gap to monitor N₂ pressure. Ultra-high purity grade nitrogen is used for the spark gap purge, while research grade purity hydrogen is used for the discharge channel.

Spark Gap Electrodes

One modification in the spark gap was the electrode design. A diagram of the new design appears in Figure 3.3. In this design, a longer, 9.5 cm piece of glass capillary was used to isolate the pulse transformer lead from the outer sleeve. This eliminated a problem associated with the old design, where a high voltage arc would often occur between the electrode sleeve and tungsten rod at the top of the electrode. The glass capillary and the W rod were sealed in place with a drop of epoxy. In order to accommodate the longer electrode, it was necessary to cut out an 8" X 5" hole from the laser cover. This hole was covered with a 9" X 6" X 5" LMB (Los Angeles, CA) utility box fastened to the cover with 6-32 screws. As a result, the spark gap spacing could be adjusted by opening the box, without the need to remove the entire cover. To attach the electrode to the pulse transformer lead located inside the laser box, a connector was formed from a 1" length of 1/4" brass round stock with a 0.04" hole drilled into the center of one face. A 2-56 threaded hole was tapped into the side to secure the W rod with a hex set screw and a 1/16" hole was drilled into the side of the piece at the other end. A length of flexible insulated wire was soldered in the 1/16" hole and the other end of the wire was fastened to the transformer lead. This custom connector was then insulated with pieces of heat shrink. By attaching the pulse transformer lead in this
Figure 3.3 Diagram of the spark gap electrode, with dimensions.
fashion, minimal torque is applied to the W rod which prevents the glass capillary from cracking.

The bottom spark gap electrode is a Cu button machined from 5/8" round stock. Thread dimensions are the same as the spark gap electrode, and two small 53 gauge holes are drilled 180° apart into the edges of the face. The ends of a surgical clamp are placed in these holes to screw the button into mating threads cut 0.160" deep in the bottom half of the spark gap assembly.

Trigger Generator

In order to generate the trigger pulse for the spark gap, a custom-built generator was employed. The circuit diagram of the generator is shown in Figure 3.4. All of the electronic components were mounted on a 7" X 19" rack panel which was bolted to a 15" X 17" X 6 1/4" aluminum frame. In order to shield the circuit from laser Rf noise, perforated aluminum sheets were bolted to each face of the frame with 10-32 screws, ≈2" apart. An RG-58 coaxial cable connects the trigger line from a BNC connector at the back of the pulse generator, to a set of banana plugs in the bottom of the laser box. The banana plugs are connected to the primary coil of a EG\&G (Salem, MS) Model TR-69 pulse generator located inside the laser box. Frequency of the trigger pulse is changed in multiples of ten with the capacitor switch and finely controlled by adjusting the 200 kΩ variable resistor. The duty cycle of the laser can be set according to calibrated positions of the frequency control knobs on the front panel or the exact frequency can be monitored from the BNC connector shown in the circuit diagram.

Laser Power Supply

A circuit diagram of the high voltage supply for the bottom Blumlein plate is shown in Figure 3.5. The heart of the system is a General Electric (Milwaukee, WI) Model 11TK18 high voltage transformer. Voltage from the transformer is controlled by a variac mounted on the
Figure 3.4 Circuit diagram of the spark gap trigger generator.
Figure 3.5 Circuit diagram for the high voltage supply of the hydrogen laser.
control panel. In order to accurately monitor plate voltage, a 1000:1 voltage divider was connected between the contact point for the laser cable, and a General Electric Model 8D091A252AC2 DC kilovolt meter (50 μA full scale) mounted on the control panel. The four lengths of ten 2.2 MΩ, 2 watt resistors were soldered together, covered with heat shrink, and mounted on a lucite sheet which was bolted inside the laser rack. In order to dampen any meter pulsations due to the rapid charging/discharging of the Blumlein plate, a 0.5 μF electrolytic capacitor was placed across the meter terminals. The meter readings were found to be accurate when checked against measurements of the plate voltage with a high voltage probe connected to a DVM. All of the high voltage connections were carefully sealed up to prevent arcing to surfaces inside the rack. Cable linkages consisting of two ring tongue connectors fastened with a bolt and nut were covered with a piece of thick-walled tygon tubing and sealed on the ends with electrical tape.

During the initial stages of this research, it was very difficult to obtain reliable triggering of the laser. The spark gap switch would often not "close" after it had been triggered. Various combinations of spark gap spacings, nitrogen pressures, and duty cycles were attempted but steady triggering could not be achieved over a period of time without a glitch every few seconds. After examining the power supply, it was suspected that the bottom Blumlein plate was charging up too quickly. The original power supply utilized a bank of fifteen 18 kΩ, 100 watt resistors for a total resistance of 270 kΩ to limit charging current of the plate. In order to measure the charging profile of the bottom plate, an experiment was carried out where a X10 scope probe was attached at the 1000:1 voltage divider shown in Figure 3.5. The meter and the .5 μF capacitor were disconnected from the circuit and the scope probe was connected to a LeCroy (Chesnut Ridge, NY) Model 9400A digital storage oscilloscope. Figure 3.6a shows the charging profile for the
Figure 3.6 Charging profiles of the bottom Blumlein laser plate with different current-limiting resistances: (a) 270 kΩ, (b) 2 MΩ. The arrows indicate the point in time when the plate is charged up to 63\% of its maximum voltage (Δt = 1 RC time constant).
270 kΩ resistor bank averaged over 100 laser pulses, with a plate
toltage of 21 kV and a duty cycle of 10 Hz. H₂ pressure in the
discharge channel was 45 torr and N₂ pressure in the spark gap was 61
psi. The arrow is located at the point in time when the plate is
charged up to 63% of its maximum voltage or 1 RC time constant. An RC
time constant of 1.3 msec was determined from this measurement. For a
270 kΩ resistance, the time for the plate to be fully charged will be
5RC or 40 msec, which would correspond to a duty cycle of 154 Hz! Based
on this analysis, it was concluded that a larger resistance was
necessary to limit plate charging for reliable triggering.

To obtain the most reproducible triggering with the highest energy
per pulse, a lower frequency, typically 10-20 Hz, must be used⁷. This
is due to the fact that higher repetition rates will require a lower
resistance for plate charging, but lowering the resistance causes
irreproducible spark gap triggering. However, a higher resistance
limits the plate from completely charging up between duty cycles of
higher frequencies, resulting in a decrease of energy per pulse.

From the RC constant experimentally determined with the 270 kΩ
resistance, a capacitance 4.8 pf was calculated for the Blumlein plate.
Assuming a desired frequency of 20 Hz, the resistance necessary to
limit charging for 5RC was calculated to be 2.1 MΩ. Therefore, the 270
kΩ resistor bank was replaced with twenty 100 kΩ, 225 watt Ohmite
(Skokie, IL) stock# 0925 resistors, as illustrated in Figure 3.5. The
resistors were mounted in a staggered formation on a 31" X 17 1/4" frame
constructed from eight 3/8" thick, 3" wide lucite planks bolted
together. Eyelets in the resistors were connected together by 8-32
screws and nuts placed through ring tongue terminal connectors fastened
to the ends of 6" lengths of heavily-insulated cable. Pieces of thick-
walled tygon tubing were then slipped over the contact points. One
distinct advantage of this design is the ability to conveniently select
a smaller resistance. The resistor bank frame was bolted to a metal strip inside the back of the laser rack. A small aluminum strip tapped with 6-32 holes attached to the base of the lucite frame served as a common connection point for the resistor network, laser cable, and voltage divider. A grounding pole was hung next to this contact point, so that the Blumlein plate and power supply could be discharged before attempting to service the laser.

After the new 2 MΩ resistor bank was in place, the above experiment was repeated to measure the charging current profile. Data for a plate voltage of 22 kV is shown in Figure 3.6b. N₂ spark gap pressure was 61 psi. From this profile, an RC time constant of 8 msec was determined, which corresponds to a maximum duty cycle of 25 Hz for 5RC. As a result of the resistor network modification, reliable triggering of the laser was finally possible. The laser was operated continuously for periods up to an hour without any glitches in triggering. In addition, maintenance was greatly simplified. Changes in the spark gap spacing, due to sputtering of the bottom electrode over time, could be easily compensated for by slightly lowering the N₂ pressure, without the need to disassemble the spark gap. After servicing the laser, the proper spark gap spacing and pressure could easily be established within ten minutes (see Appendix B). Once the correct spacing was determined, the laser could be used over a period of several months with only the need to occasionally adjust the N₂ pressure from time to time.

Laser Output

Output of the H₂ laser for the Lyman transitions in the VUV is shown in Figure 3.7. This data was previously recorded by Babis⁷ from a film emulsion placed at the Rowland circle of a vacuum-ultraviolet polychromator. The intense cluster of lines around 160 nm correspond to 7.8 eV photons from the source which are utilized for single-photon
Figure 3.7 Spectral output of the hydrogen laser measured with a VUV polychromator, from Ref. 73. Wavelength values are in nanometers.
ionization mass spectrometry. A pulse energy of 30 μJ has been measured for these lines\textsuperscript{6}. To date, no lasing action for Werner bands has been reported for the particular design used in this study.
CHAPTER 4

INSTRUMENTATION: THE TIME-OF-FLIGHT MASS SPECTROMETER

To evaluate the hydrogen laser source for mass spectrometry, a linear time-of-flight (TOF) mass analyzer is used, which is based on the design of Wiley and McLaren. The TOF system is capable of acquiring a complete mass spectrum with each laser pulse, in contrast to scanning systems such as quadrupole and magnetic sector mass analyzers. Ion collection efficiency of TOF can be as high as 50% versus 5% for typical scanning instruments. In addition, the TOF instrument is a simple, inexpensive device and is easy to use. A block diagram of the instrument used in this study is shown in Figure 4.1 and a schematic representation of the system is illustrated in Figure 4.2. Ions formed with each laser pulse are accelerated from the ion source into a field-free drift tube and directed towards a detector placed at the end of the tube. To a first approximation, a packet of ions having the same mass $m$, that have been accelerated to a potential $V$, acquire a velocity $v$ related by:

$$v = \left( \frac{2neV}{m} \right)^{1/2}$$  \hspace{1cm} (1)

where $n$ is the charge of the ion in Coulombs. For a drift region of length $L$ (in meters), the ion flight time will be:

$$t_f = \frac{L}{v} = L \left( \frac{m}{2neV} \right)^{1/2}$$  \hspace{1cm} (2)

Therefore, ion packets will arrive at the detector separated in time according to their masses, lighter ions arriving first, followed by heavier ions.

Samples are introduced into the ion source through injections into a heated inlet or from a solid sample probe. VUV radiation from the H$_2$
Figure 4.1 Block diagram of the hydrogen laser/TOF mass spectrometer system.
Figure 4.2 Schematic diagram of the photoionization mass spectrometer.
laser is directed into the ion source through a purge tube filled with helium, and photoionized molecules are accelerated into the 1.5 m flight tube from electrodes in the ion source. A cylindrical lens and pickup lens serve to focus the ion packets onto the aperture of a magnetic electron multiplier. Current pulses from this detector are then amplified by an electrometer and sent to a digital storage oscilloscope, which can average mass spectra over many laser pulses. Synchronization of the oscilloscope trigger with each laser pulse is accomplished by a pulse generator triggered from the burst of Rf noise coupled into an antenna. An IEEE-488 interface links the host computer with the oscilloscope for waveform acquisition, storage, and analysis.

The basic design and construction principles of the TOF mass spectrometer system used in this study have been discussed previously. However, many modifications have been made and therefore, the design of the system will be reviewed here.

The Vacuum System

The ion source housing, detector housing, and flight tube are all constructed from 4" Dependix (Anaon, Burlington, MA) stainless steel vacuum components. These components are connected and terminated with mating flanges which contain a large O-ring seal. The ion source housing was a Tee section customized with a 3/4" Cajon (Macedonia, OH) Ultra-Torr fitting welded on the side for the laser purge tube and an identical fitting welded on top for the sample inlet. The ion source and flight tube were connected together with a 4-way cross section, which was bolted to a custom 11" o.d. aluminum flange with a 4" hole, located at the top of the diffusion pump stack assembly. This assembly consisted of a Varian (Palo Alto, CA) Model VHS-6 6" diffusion pump, a liquid N$_2$-cooled cyroaffle (CVC Products, Inc., Rochester, NY), a manually operated gate-valve (Vacuum Research Company, Chicago, IL), and an 11" o.d., 3 3/8" high custom flange, sealed together with 3/4" bolts.
The custom flange below the flight tube contained a roughing line and a sending element for a thermal conductivity gauge (MDC Vacuum Products Co., Model TCC-200, Hayward, CA), for monitoring rough vacuum. A Varian Model 1251 manually-operated bellows valve was connected to the end of the roughing line to draw a vacuum on the chamber, before opening the gate valve. An identical valve was attached to the diffusion pump foreline. The chamber roughing valve was linked to the foreline with Kwik-Flange (MDC Vacuum Products Co.) 1.5" o.d. vacuum components. A Kwik-Flange Tee section was placed beyond the foreline valve, which contained a 3/8" o.d. stainless steel tube threaded into a mating flange. This assembly provided a roughing port for the sample probe inlet. A molecular sieve trap was placed in the foreline and connected to a Kinney (Boston, MA) Model KC15 mechanical rough pump with a 19" section of 3" o.d., 1.5" i.d. rubber hose (Dunaway Stockroom Corp., Mountain View, CA), which served to dampen vibrations from the pump. A Veeco (Plainview, NY) Model RG-81 ionization controller is used to monitor high vacuum in the flight tube from an RG-75N gauge tube mounted in the roughing line between the top of the chamber and the roughing valve.

In order to bake out the vacuum system, the flight tube and detector housing were wrapped with 1" wide standard fibrox heating tape (Thermolyne Co., Dubuque, IO). Since the tape was not recommended for direct contact to metal surfaces, it was necessary to wrap a strip of ceramic fiber tape over the surfaces before placing the heating tape down. A strip of 1/2" wide heating tape was also wrapped around the roughing line at the top of the chamber. Current was supplied to the heating tape strips by three Powerstat (Superior Electric Co., Bristol, CN) Type 116B variable autotransformers. The vacuum system was typically heated to ~80 °C during a bake-out cycle.

The rough pump was bolted to a .5" thick sheet of aluminum (30" X
20") mounted on casters, to absorb vibrations. To support the diffusion pump stack and flight tube, two aluminum plates were bolted to the diff pump base, which were fastened to the short edges of two 28 3/8" lengths of 4" channel steel, notched on each end. The 4" channel steel supports were bolted in the center of a 3' X 28.5" X 2' support frame constructed from pieces of 3" channel steel welded together. A custom vacuum controller was constructed, based on the circuit shown in Figure 4.3. The circuitry contains fuse protection for both vacuum pumps and a size 00 motor contactor (Allen-Bradley, Cat# 509-TAH, Milwaukee, WI) for the rough pump motor. The fuses, phase indicator lights, and diff pump relay were all mounted inside a 1' X 1' X 6" steel electrical box (Allen-Bradley). The electrical box and motor contactor were mounted on a 20" X 1', 3/8" thick aluminum plate which had a series of 10-24 screw holes tapped into the top edge. This plate was then mounted under a 28.5" X 10" plate bolted across the top of the diffusion pump frame, on the left side. A 10" X 8" X 3" aluminum utility box (LMB, Los Angeles, CA) served as the housing for the vacuum pump controls. The box was mounted to the top of plate, underneath the gate valve, and a hole was drilled into the center of the box and through the plate for the control wires. All of the switches and indicator lights were mounted to the cover of the utility box, along with the thermal conductivity meter. Operation of the diffusion pump is interlocked to the rough pump in order to prevent accidental operation of the diff pump without a vacuum on the foreline. In the event of a power failure, the diffusion pump will remain off until it is manually reactivated, while the rough pump will resume operation when power is restored. 

**Coupling The Laser Source With The TOF Mass Spectrometer**

Previously, the laser source was mounted on a separate frame welded together from pieces of 1 1/4" angle iron and the frame was placed behind the ion source of the TOF mass spectrometer. The base of
Figure 4.3  Circuit diagram of the vacuum system controller.
the frame was then secured in place with lead bricks. However, the old frame design was poor, since the frame was very flimsy and it was difficult to keep the laser properly aligned. Any slight movement in the vacuum support frame or the laser frame would cause an alignment problem, since each frame was independent. In addition, the laser frame was very awkward to work with when it became necessary to make repairs on the device. Therefore, a new sturdy laser frame was designed and custom built, which bolted directly to the existing stand which supports the diffusion pump stack and flight tube of the mass spectrometer. Photographs of the frame are shown in Figure 4.4. The laser box is mounted on a rectangular frame constructed from four pieces of 2" wide angle steel, welded together. Slotted holes were milled into the face of the frame for adjusting the laser source height. This inner frame is mounted vertically inside a larger, outer frame with a set of two 3" channel steel arms welded to each long side of the smaller frame. The arms contain slots for 5/8" bolts, and an aluminum spacer block with a 5/8" hole in the center was custom fitted inside the channel of each arm. The outer rectangular frame was built from four lengths of 3" channel steel welded together. A notch was cut out of the bottom piece to mount the outer rectangular frame over the top cross support of the diff pump frame. Two cross supports for the outer frame were custom built from 3" channel steel cut 45° at each end, with pads of steel strap welded on both ends. A bottom support was attached vertically from the base of the diff pump stand to a section underneath the back corner of the outer frame. A side support was bolted in the horizontal plane from the right-hand side (bottom corner) of the rectangular frame to the far right corner of the mass spectrometer stand. To stabilize the top (front) corner of the outer frame, it was necessary to fasten a cross support at a 45° angle, from the right-hand side of the top corner, to the 4" channel piece bolted inside the pump stand. This
Figure 4.4 Photographs of the laser frame: top photo—laser in the vertical position for normal operation, bottom photo—laser rotated to the horizontal position for maintenance.
cross support was made from a length of 2" wide angle steel. Dimensions of the two rectangular frames were 43" X 29 7/16" for the outer frame and 37" X 23 7/16" for the inner frame.

Alignment of the laser in the horizontal plane was achieved by loosening the four bolts securing the slotted arms of the inner frame to the outer frame. One unique advantage of this design is the fact that the bolts from the two top arms can be removed and the laser box can be pivoted to a horizontal position for servicing the Blumlein apparatus. This is illustrated in the photographs of Figure 4.4.

Since the improved frame design moved the laser closer to the ion source, it was necessary to design a new purge tube, to direct laser radiation from the discharge channel into the ion source. A diagram of this purge tube is shown in Figure 4.5. All of the flanges shown were custom machined from 2" diameter brass round stock with a 3/4" hole drilled in the middle. The brass spool to the right of the diagram sealed a VUV 1" CaF$_2$ window to the face of the discharge channel and a brass nozzle was threaded into the bottom of the spool for the purge gas inlet. A mating flange was silver soldered to one end of a 3.5" long stainless steel bellows (MDC Vacuum Products Co., Model FB-6513, Hayward, CA). The other end of the bellows was silver soldered to a custom made flange that sealed another 1" CaF$_2$ window inside the cavity of a mating flange, which slipped into the 3/4" Cajon (Macedonia, OH) Ultra-Torr fitting at the entrance of the ion source. A 1/8" brass swagelock fitting was screwed into the bottom of the flange (to the left of the bellows) which was connected to a Nupro Model S-SS2-A (Willoughby, OH) fine metering valve to control the flow of purge gas in the tube. The purge tube inlet was connected to a cylinder of He with a length of tygon tubing and a 2 μm nylon filter tube (Cole-Palmer Instrument Co., Cat# L-02909-30, Chicago, IL) was placed in the gas line at the regulator. In order to prevent the CaF$_2$ window near the ion
Figure 4.5 Diagram of the purge tube interface between the hydrogen laser and the ion source of the TOF mass spectrometer.
source from heating up when heat was applied to the source housing, a 5.5" cooling fan (Air-Marine Motors, Inc., Model B7565, Amityville, NY), was mounted over the brass flange containing the window cavity.

In the previous purge tube design, a 1" CaF$_2$ planoconvex lens with a 257 mm focal length was placed at the ion source. It was rationalized that, since this lens would focus the VUV radiation to a point beyond the ion source, the beam would always be converging as it passed through the source, therefore reducing the possibility of the radiation generating photoelectrons from striking metal surfaces inside the source. To test this rationale and examine the beam profile at the ion source, a custom purge tube for the H$_2$ laser was constructed from lucite. The purge tube, shown in a photograph in Figure 4.6, contained a 2" movable screen mounted on two 6-32 threaded posts. This screen was machined from a 2" diameter piece of lucite round stock with a shallow well, 1.5" in diameter, cut in the face. The well was then packed with sodium methyl salicylate from a methanol slurry. With the screen placed at a position which corresponded to the middle of the ion source, the CaF$_2$ planoconvex lens was inserted in the cavity of the custom-made brass flange (see Figure 4.5) and placed inside the tube, on a lucite mount, which centered the 3/4" aperture over the screen. The planoconvex lens was placed at various distances from the screen with the laser firing and the result was that the laser radiation was severely defocused at all distances, with no change in the beam height. The lens was substituted with a 1" dia. 2 mm thick CaF$_2$ window, and the resulting image from the discharge channel was very sharp, consisting of a single bright slit image with a narrow dark region and another fainter slit image to the right. This image is due to the "waveguide" effect of the narrow discharge channel, where reflections of the VUV radiation off the glass surfaces in the channel produces an interference pattern. Raising the H$_2$ pressure in the discharge channel above 50 torr reduced
Figure 4.6 Photograph of lucite purge tube with fluorescent screen.
the pattern to a single image, but the intensity of fluorescence emission was substantially reduced as well. Using a ruler mounted next to the salicylate screen, the laser image from the 3/4" aperture of the window mount measured 18 mm X 2 mm at the center of the ion source. Since the ion source electrode plates, centered over the entrance window, were 2" in height and 1/2" apart, it was concluded that the laser beam should still clear the electrodes with a simple CaF₂ window in place. Therefore, since the planoconvex lens served no useful purpose and defocused the VUV radiation, it was replaced with a 2 mm thick 1" dia. window, as shown to the left of Figure 4.5.

From the H₂ laser beam profile measured above, an effective area of .36 cm² was calculated at the center of the ion source. Assuming a pulse duration of .8 nsec and the previously measured average pulse energy value of 30 μJ, estimated laser power at the source would be approximately 100 kW/cm².

Since the ion source electrodes were centered between the laser entrance and exit ports of the source housing, a custom flange with a 2" diameter CaF₂ window at 45° angle, provided an exit for the laser beam. This flange, described previously, was designed to direct radiation downward, rather than back into the ion source. In order to initially align the laser beam with the source, this flange was replaced by the custom-built flange shown in Figure 4.7, which contains a 1" dia. quartz window, coated with phosphor on the side facing the ion source and sealed between two O-rings in a 1" Cajon Ultra-Torr fitting. With the chamber at rough vacuum, and the laser firing, adjustments were made in the laser frame mounts until the beam was aligned in the center of the phosphor-coated window. Then this flange assembly was replaced with the flange containing the 45° CaF₂ window, before pumping the chamber down to high vacuum.
Figure 4.7 Diagram of flange assembly used to align the hydrogen laser beam within the ion source of the TOF mass spectrometer.
Ion Optics and Theoretical Background of The Linear TOF Mass Spectrometer

The ion source, described previously\(^7\), was constructed from Kimball Physics (Wilton, NH) eV parts, with electrodes made from 2" square stainless steel plates. Figure 4.8 contains an illustration of the mass spectrometer with the dimensions of the accelerating fields and drift tube. The first field \((E_s)\) electrode is a solid plate separated by a distance \((s)\) of 1.27 cm from the second field \((E_d)\) electrode, which is a plate with a fine tungsten grid spot welded over an oval aperture, 2.54 cm \(\times 0.5\) cm. The distance \((d)\) of the second field is defined by a parallel plate at ground potential with a tungsten grid over a 1" dia. hole, located 1.0 cm away from the second electrode. Directly in front of this aperture is a set of three 1" dia., 1.5" long cylinders, mounted on parallel 2" plates, which make up the lens to focus ions onto the detector. A focusing potential was placed on the center cylinder, while the end cylinders were held at ground potential. The entire ion source assembly was mounted on a custom-made aluminum flange with BNC feedthroughs for the electrode voltages. For the time-of-flight mass spectrometer illustrated in Figure 4.8, an ion formed in the source with an initial translational energy \(U_o\), will be accelerated to a total energy \(U\), described by:

\[
U = U_o + qSE_s + qdE_d
\]  \(\text{(3)}\)

Therefore the flight time will be the sum of times it takes the ion to travel through each region or:

\[
T(U_o, s) = T_s + T_d + T_D
\]  \(\text{(4)}\)

where each time is defined by:
Figure 4.8 Diagram of the linear time-of-flight mass spectrometer, with field parameters and dimensions.

\[ s = 1.27 \text{ cm} \quad d = 1.00 \text{ cm} \quad D = 145 \text{ cm} \]
\[ T_s = 1.02 \frac{(2m)^{1/2}}{qE_o} [(U_o + qSE_s)^{1/2} \pm (U_o)^{1/2}] \]  

(5)

\[ T_s = 1.02 \frac{(2m)^{1/2}}{qE_d} [U^{1/2} - (U_o + qSE_s)^{1/2}] \]  

(6)

\[ T_D = 1.02 \frac{(2m)^{1/2}D}{2U^{1/2}} \]  

(7)

The ± sign in the \( T_s \) term is due to the fact that an ion velocity can be directed toward or away from the detector. If \( U_o = 0 \), and the ion is formed in the center of the first field \( (s = s_o) \), a constant, \( k_o \), can be defined as:

\[ k_o = \frac{s_oE_s + dE_d}{s_oE_o} \]  

(8)

and total flight time of the ion \( T(0,s_o) \) is derived as:

\[ T(0,s_o) = 1.02 \left( \frac{m}{2U} \right)^{1/2} \left( 2k_o^{1/2}S_o + \frac{2k_o^{1/2}d}{k_o^{1/2} + 1} + D \right) \]  

(9)

In the first field region of the ion source, ions will be formed at various positions inside a region defined by the laser beam width, \( \Delta s \). Ions formed closer to the backing plate electrode \( (s = s_o + \frac{1}{2}\Delta s) \) will experience a greater potential than ions formed closer to the detector \( (s = s_o - \frac{1}{2}\Delta s) \). The focusing condition of the spectrometer can be defined by determining the distance in the field-free region where ions in the former case will overtake ions of the latter case. This is accomplished by setting the derivative \( (dT/ds) \) of Equation 4 equal to zero and solving for \( D \):
\[ D = 2s_0 k_0^{3/2} \left( 1 - \frac{d}{s_0 (k_0 + k_0^{1/2})} \right) \]  

In order to determine the correct accelerating voltage \( V_d \), to satisfy the focusing condition of the mass spectrometer used in this study, a simple program was written for iterative solving of Equation 10 (See Appendix C). Since the voltage supply for \( V_d \) is a 45 V battery (see below) and the other parameters \( s, d, D, s_0, \) and \( \Delta s \) are all fixed by the spectrometer design, the accelerating potential is the only variable. For the values given in Figure 4.8, with a laser beam width \( \Delta s \) of .2 cm measured earlier, an accelerating voltage of 526 V was determined for the focusing condition.

Resolution of the TOF mass spectrometer is determined by two factors, space resolution and energy resolution. Space resolution corresponds to the change in flight time, \( \Delta T \) for ions formed in the space, \( \Delta s \) defined by the laser beam. This change in flight time is represented by Wiley and McLaren as the series expansion of \( T(0,s) \) about \( s_0 \):

\[ \Delta T_{\Delta s} = \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{d^n T}{ds^n} (0,s) \right)_{s_0} (\Delta s)^n \]  

The measure of space resolution, \( N \), is the maximum ion mass, \( m \) where adjacent masses are separated in time or \( \Delta T_{\Delta s} \leq T_{m+1} - T_m \). This separation in time for adjacent masses is derived from Equation 9:

\[ T_{m+1} - T_m = \left[ \left( 1 + \frac{1}{m} \right)^{1/2} - 1 \right] T_m = \frac{T_m}{2m} \]  

By substituting \( \Delta s/2 \), the maximum deviation of \( s \) from \( s_0 \), in Equation 11 for \( \Delta s \), and making the assumptions that \( k_o \gg 1 \) and \( k_o \gg d/s_o \), Wiley and McLaren derived the following expression for space resolution from Equations 9, 11, and 12:
\[ M_s = 16k_s \left( \frac{S_o}{\Delta S} \right)^2 \]  

(13)

Energy resolution is due to the fact that ions formed in the source will have different initial translational energies in accordance to a Maxwell-Boltzmann distribution. The time spread, introduced by the initial ion energies, is the time it takes for an ion traveling away from the detector to be decelerated and turned around. Ions with velocities directed away from the detector will lag ions with velocities directed toward the detector by this "turn-around" time. Therefore the time spread, \( \Delta T_s \), will be the "turn-around" time for an ion with the maximum initial energy:

\[ \Delta T_s = 1.02 \frac{2V_{dm}}{qE_o} = 1.02 \frac{2(2mU_o)^{1/2}}{qE_o} \]  

(14)

The maximum resolvable mass, \( M_s \), will be the mass of ions whose time spread, \( \Delta T_s \), equals the time between adjacent mass peaks, \( T/2m \). Wiley and McLaren derived the following expression for \( M_s \) from Equations 9, 10, and 14:

\[ M_s = \frac{1}{4} \left( \frac{U_c}{U_o} \right)^{1/2} \left( \frac{k_o + 1}{k_o^{1/2}} - \frac{k_o^{1/2} - 1}{k_o + k_o^{1/2}} \frac{d}{S_o} \right) \]  

(15)

The overall resolution can be obtained by assuming that the total spread in flight times for an ion packet will be the sum of the spreads from the space and energy terms:

\[ \frac{1}{M_{s,0}} = \frac{1}{M_s} + \frac{1}{M_o} \]  

(16)

One way of eliminating space focusing as the limiting factor in determining the overall resolution, is to make \( s \) large with respect to \( s_o \) by spreading the electrodes of the ion source apart. For the mass...
spectrometer used in this study, a value of approximately 4,000 amu was calculated for \( M_n \) where \( k_n \) is 24. Therefore, space broadening of the ions is negligible compared to the dominate effect of energy broadening.

A method of improving energy resolution as demonstrated by Wiley and McLaren is to introduce a time lag between ion formation and application of an ejecting pulse to the backing plate. A time-lag will exist at which ions will spread out to new positions where ions with maximum velocity, directed away from the detector, will experience a large enough potential to turn around and overtake the other ions (with initial velocity directed toward the detector) as the ion packet arrives at the end of the drift tube. This time-lag, is approximately one-half the turn-around time calculated from Equation 14:

\[
\tau = \frac{-1.02m}{qE_s \frac{dT}{ds}}
\]  \hspace{1cm} (17)

Since the proper time-lag will be dependent on the ion mass, one significant disadvantage of this approach is that only a narrow mass region will be focused for a particular time delay, while the rest of the ion peaks in the spectrum will be defocused.

A variety of alternate methods for improving resolution in TOF mass spectrometry have appeared in the literature. One approach is the use of a reflectron\(^{8}\), where the energy spread in an ion packet is corrected by reflecting the ions through a static electric field prior to their arrival at the detector. An additional advantage of this approach is the ability to increase the resident drift time of the ions, which also improves resolution. Another approach to correct for the energy spread of isomass ions is velocity compaction\(^{9}\), in which a voltage ramp with respect to time is applied to a third accelerating field at a distance from the ion source. Recently, a new technique of post source pulse focusing has been reported\(^{10}\), where a focusing voltage
pulse is applied to a short field-free region located beyond the source, after the ions have entered this region.

The accelerating potential \( (V_d) \) for the ion source electrodes was supplied from a Nuclide Co. (State College, PA) Model HV-5 variable DC high voltage supply. In order to generate the voltages for the first and second field electrodes, the output of the high voltage supply was coupled into a shielded box containing a custom pulse generator circuit\(^2\), with a \( 45 \) V \( (V_1) \) battery supply (Eveready, No. 415, St. Louis, MO). The externally-triggered pulse generator was capable of adding a \( 45 \) V flat-top pulse to the first field electrode, which is floated at the accelerating voltage \( (V_d) \). This pulse lasted \( =2 \mu \text{sec} \) with a risetime of \( =150 \) nsec. The circuit contained a variable delay for the \( 45 \) V pulse which could be adjusted from \( 1.5 \mu \text{sec} \) to \( 8 \mu \text{sec} \), for time-lag focusing. A modification of the circuit was made with the addition of a three-position switch so that the \( 45 \) V supply could be added to the backing plate electrode in either a static mode or a pulsed mode. When the instrument was not being used, the switch was placed in the "OFF" position, which disconnected the battery from the circuit. The box containing the pulse generator circuit was mounted on a 19" panel with BNC connections for a trigger input and the output voltages \( (V_d + V_1 \) and \( V_d) \) for the ion source electrodes. The high voltage supply and pulse generator box were mounted inside a \( 19" \) rack, 3' high and 18" deep.

Voltage for the cylindrical focusing lens was provided from a Hammer Electronics Co (Princeton, NJ) Model HV-13 high voltage DC supply. This supply was mounted inside a \( 19" \) rack, 40" high and 25" deep along with the power supplies for the pickup lens and detector.

A pick-up lens, described previously\(^5\), was used to focus ions onto the cathode of the electron multiplier. This lens, located at a distance 21.6 cm from the detector, was constructed from three \( 2" \) plates with \( 1" \) apertures. The lens was mounted on a custom-made aluminum flange
with the end plates grounded to the flange and the middle plate wired to a BNC feedthrough connector. Voltage to the lens was supplied from a Heathkit Co. (Benton Harbor, MI) Model IP-7 DC power supply.

**Ion Detector and Preamplifier**

The ion detector used in the initial stages of this study was a Galileo Electro-Optics (Stubridge, MA) M-306 magnetic electron multiplier (MEM). This detector contains an entrance grid, a tungsten cathode, two glass plates with a high resistance coating, and a stainless steel collector anode, all surrounded by a set of magnets. One glass plate serves as the field strip, while the other serves as the dynode strip. High voltage applied across the inputs of the glass strips produces a gradient which gives rise to an electron cascade along the length of the strips when ions strike the cathode. The magnetic field directs the cycloidal motions of the electrons along the strip. For proper electron multiplication, the field strip must always be positively biased with respect to the dynode strip. Therefore, in order to set an arbitrary potential difference of 300 V for the dynode strip with respect to the field strip, 10 MΩ resistors were placed between the output and input ends of the strips. The detector was mounted vertically on a custom-made aluminum flange and placed in the Tee vacuum housing at the end of the flight tube, so that the cathode was centered with the ion optics. BNC feedthroughs on the flange provided connections for the high voltage input, anode output, and field strip output (ground).

After a period of operation, the glass strips of the MEM will become dirty due to electron beam deposition of hydrocarbon material near the output end, which gives rise to excessive detector noise. The detector must be disassembled and the plates are cleaned by gently rubbing a "Pink-Pearl" type eraser across the glass surface. All the detector parts are then taken through a vacuum wash of benzene, acetone,
water and ethanol before reassembling the device.

The high voltage input of the detector was connected to a Nuclide Co. (State College, PA) Model EM-3A power supply. To monitor the detector voltage, the output of the supply was also connected to a 5 MΩ resistance attached to a 1000 Ω/V voltage meter (5 V full scale), mounted on a 19" rack panel above the power supply.

For amplification of current pulses from the detector, a custom 2-stage high frequency electrometer was designed. Before designing and constructing this preamplifier, two electrometers, which had been previously custom-built for the TOF system, were examined. One of these electrometers, which was found connected to the TOF instrument, contained a circuit with a single NE5539 ultra high frequency operational amplifier chip, operating in an open-loop gain mode. The other electrometer, discussed previously, contained a 2-stage amplifier circuit with NE5539 chips. Both electrometer circuits were housed inside 4" X 2.75" X 2" aluminum BUD boxes with BNC connections at each end for the input and output. Power for the circuits was provided from a custom-built +12 and -12 volt supply. Both of these devices were tested by sending current pulses from a Hewlett Packard (Palo Alto, CA) Model 222A pulse generator into the input through a 10 kΩ resistor. Pulse widths were varied between 100 nsec (FWHM) and 1 usec with current amplitudes from a few tenths of a μamp to 100 μamps, to simulate current pulses typically produced from the detector during normal operation of the spectrometer. The input and output pulses were then simultaneously observed with an oscilloscope. For the single-stage device operating in an open-loop gain mode, severe distortion of the current pulse was observed, with a very long fall time for the output pulse. While the previously designed 2-stage circuit showed minimal pulse distortion for low current inputs (in the μamp range), the device had little dynamic range and was driven into saturation for current pulses higher than
=6 μA. Since typical ion pulses from the detector were on the order of
tens of microamps, this device was unacceptable for quantitative
studies. Therefore a new custom-made 2-stage electrometer was
constructed.

The circuit diagram of this device is shown in Figure 4.9. For
building the circuit, it was recommended in the NE5539 amplifier
literature to use a double-sided copper clad circuit board. Therefore,
a pattern for the circuit was traced onto a sheet of typing paper taped
over a perforated circuit board, to ensure proper spacing of the holes
for components such as the 8-pin sockets for the amplifier chips. Then
this pattern was taped across a 7" X 4" double-sided blank copper
circuit board. Holes for the components were drilled into the board
with a 60 gauge drill on a mini drill-press. The paper was removed and
the pattern was traced on the backside of the board with an Archer (Cat# 276-1530, Radio Shack, Fort Worth, TX) resist marking pen, to provide
soldering pads and connections for the components. On the component
side, circles were drawn around the holes and the area between the
circles was filled in to provide a ground plane on this side. The
borders along the edges of the board were sealed off with masking tape
and the board was immersed in an FeCl₃ etching solution (GC Electronics
Co., Rockford, IL) heated on a hot plate. Then the board was cleaned
and immersed in a bath of tin plating solution (GC Electronics Co.,
Rockford, IL). Once all of the components were soldered in place, the
board was mounted in the bottom of a 7 7/8" x 4 3/4" x 2 1/8" die cast
aluminum BUD box (LBM, Willoughby, OH), which was fitted with a female
BNC connector on one end and a male BNC connector on the other for the
input and output. A male 9-pin D connector mounted on one side of the
box provided +15 V, -15 V, and ground connections to the custom power
supply. The power supply was plugged into an extension cord containing
a set of Rf line filters (Model GF-2045-8, Genistron, Inc., Los Angeles,
Figure 4.9 Circuit diagram of the custom-built two-stage preamplifier.
CA), to isolate the electrometer from Rf noise. In order to measure the current pulse characteristics of the new preamplifier, the experiments above were repeated. The new device had a linear response from a few tenths of a µamp to 150 µamps for pulse widths of 100 nsec or greater (FWHM), with no significant distortion.

Data Acquisition

Previously, mass spectral data was obtained by taking photographs of an oscilloscope screen with Polaroid Type 47 film (ASA 3000), where the film was exposed to the screen over 500-1000 laser pulses\(^7\). This method was a very tedious procedure, requiring timed development of the photograph after exposure. Exposure and development time would vary depending on the temperature and age of the film. Overexposure of the film was always a possibility and if the photograph did not turn out, the experiment had to be repeated. In addition, there was no means of observing the trace once the shutter of the camera had been opened. Therefore, a considerable amount of guesswork was involved in determining optimum exposure time and the correct starting point when ion signals were near their maximum intensity. Finally, quantitative aspects of the laser photoionization technique, such as measurement of detection limits, could not be evaluated due to limitations associated with photographic methods.

For proper data acquisition and storage of mass spectra, a number of electronic waveform recording devices were considered. These included digital storage oscilloscopes, transient digitizers, and fast data acquisition boards which plug directly into the bus of a personal computer (PC). Ideally, the device should have a memory storage buffer large enough to record an entire mass spectrum, with a high sampling rate and a broad analog bandwidth to accurately record each ion peak. In addition, the device should have such features as signal averaging, variable amplification, and a computer interface for mass storage and
data analysis. Finally, the device should be affordable and easy to use. Transient digitizers, while having ideal waveform recording for time-of-flight and excellent computer software packages, are cost prohibitive. High speed data acquisition PC boards, on the other hand, are in their infancy with respect to offering the advanced features of transient digitizers or digital storage oscilloscopes. While these boards represent the most inexpensive solution, digital oscilloscope emulation software packages are limited with respect to applications in time-of-flight. The alternative is to design custom-written programs in higher level languages, such as C, to control the board, but iterative execution of these programs necessary to arm the board and move the waveform in memory limit data throughput rates, which are crucial for pulsed-laser TOF experiments. In addition, real-time display of waveforms with each trigger on a PC screen will be limited to a very short segment of data points at low repetition frequencies, due to computer hardware.

Digital storage oscilloscopes probably represent the best overall compromise with respect to cost and performance. For the initial stages of this project, a Tektronix (Beaverton, OR) Model 2430 digital storage oscilloscope was on loan from another research group. This instrument had a 100 MHz analog bandwidth with a sampling rate which varied with the time base setting. For a 10 μsec/div time base (necessary to acquire a complete mass spectrum), the sampling frequency of the 8 bit analog-to-digital flash converter was 25 MHz (40 nsec/point). The scope had the ability to store three 1024 point waveforms in its 4K of memory and contained a IEEE-488 port for computer control and data transfer. Waveforms could be averaged over 256 laser pulses before storage into the buffer memory.

Once a waveform was stored in the scope's memory, the data was transferred to a 20 MHz IBM AT compatible computer via a Capital
Equipment Co. (Burlington, MA) Model CEC-488 general purpose-interface bus (GPIB) card equipped with 8 K cache RAM. Data acquisition and analysis programs were written for the digital oscilloscope using the ASYST (ASYST Software Technologies, Inc., Rochester, NY) version 3.0 scientific software package with the GPIB (Module 4) option. ASYST is an I/O FORTH type programming language. For a listing of the custom-written ASYST software routines, refer to Appendix C.

Synchronization of the oscilloscope sweep and ion source repeller pulse with each laser shot was accomplished by Rf noise triggering of a Hewlett Packard (Palo Alto, CA) Model 222A pulse generator, as illustrated in Figure 4.1. An antenna circuit was placed at the trigger input of the generator, which consisted of a 20 pF ceramic disk capacitor soldered in parallel with a 22 kΩ resistor, with the N lead of a crystal diode soldered to one end. This end was placed into a BNC banana plug screw terminal (Pomona Electronics Co., Pomona, CA), which was connected to the trigger input, and an alligator clip with a short length of wire was fastened to the P end of the crystal diode, to act as the antenna. Once the Rf noise burst from the laser triggered the pulse generator, a 5 V, 4 μsec wide pulse from the generator was sent to the oscilloscope and the repeller pulse generator. A delay of a few microseconds was usually set on this triggering pulse, so that the two devices would receive a clean trigger after the initial burst of Rf noise from the laser. By observing the laser Rf burst and trigger pulse on a digital oscilloscope, it was determined that jitter associated with triggering was no greater than 1 nanosecond.

Sample Introduction

For injections of solutions into the ion source of the mass spectrometer, the custom inlet shown in Figure 4.10 was used. This inlet was constructed from 1/16" stainless steel tubing and swage lock fittings connected to an SGE (Melbourne, Australia) Model MNVU-50 fine
Figure 4.10 Heated inlet for introducing solutions into the ion source of the TOF mass spectrometer.
metering valve. The injection port was a 1/16" to 1/4" swagelock adapter with a custom-made brass insert silver soldered to the face of the 1/4" end. This insert, designed to reduce dead volume, had a 0.04" hole drilled through the center to guide the syringe needle into the 1/16" tubing. A 3/8" brass disk with a 1/16" hole was placed into a 1/4" swagelock nut along with a high-temperature silicone septum (Supelco Inc., Bellefonte, PA) and the nut was fastened to the swagelock adapter to seal the septum between the two brass pieces. The base of the heated inlet was machined from a 1 7/8" piece of 3/4" diameter brass round stock. A 5/8" hole was drilled halfway into one face and a 1/16" hole was drilled through the other face, for the tubing feedthrough. A length of 1/16" tubing was passed through the hole and silver soldered at the top of the base. The base was fitted with a custom aluminum frame to support the injection port and the valve stem. A type J thermocouple was attached to the base and the inlet was wrapped with a Glas-Col (Terre Haute, IN) Model SCC4 heating cord. The inlet was placed into the 3/4" Cajon Ultra-Torr fitting at the top of the ion source and the remaining length of the cord was wrapped around the source housing. Solutions were introduced into the inlet with a Hamilton Co. (Reno, NV) Model 701-N microliter syringe.

In order to heat the inlet and/or ion source, a custom temperature controller was constructed. Schematic diagrams of the controller circuit and power supplies are shown in Figures 4.11 and 4.12. Components of the controller circuit were placed on a breadboard and wire-wrapped together. The heart of the controller circuit is an Analog Devices (Norwood, MA) AD594 thermocouple amplifier chip which outputs a 10 mV/°C signal. This signal is fed into a comparator circuit, which turns on a solid state relay for the heating tape when the chip output falls below the voltage of the temperature set point controller. Thermocouple temperature was monitored with a digital panel meter (Model
Figure 4.11 Circuit diagram of the custom-built temperature controller.
Figure 4.12 Circuit diagram of power supplies for the temperature controller.
DPM-035A, Electronic City, Tucson, AZ), connected to the chip output via a 1000:1 voltage divider. Power for the controller circuit was provided by a Jameco Electronics (Belmont, CA) Model JE215 dual power supply, adjusted for +15 V and -15 V. Current to the heating cord was regulated with a standard 120 VAC dimmer switch, placed between the relay and heater outlet. The temperature controller was housed in a 7" X 6" X 4" aluminum box with walnut panels on the 4" sides (Energy Engineering Inc., Fayetteville, AK). The temperature meter, thermocouple input jack, power switch, and temperature control knob were mounted on the front of the box, along with the "thermocouple open" and "heater on" LED indicators. The heater outlet, fuse holders and power cord were located on the backside, while the dimmer switch was mounted on the top side.

The temperature reading of the controller was calibrated with a lab thermometer suspended in a beaker of boiling distilled water. Once the controller was in operation, the dimmer switch was adjusted until the heater turned on and off with an equal cycle time. The custom controller had excellent precision, maintaining temperature of the ion source within ± .5 °C, even at elevated temperatures greater than 200 °C.

Previously, solid residues were introduced into the ion source with a custom-built sample probe, where a small sample vial was heated by wrapping a piece of nichrome wire around the vial and probe tip. However, this design proved to be very cumbersome to work with. Since the vial was only supported by windings of nichrome wire wrapped around the vial and the probe, the vial would often slip out when the probe was pushed through the custom inlet. For each sample run, the old wire had to be disconnected and a new length of wire had to be wrapped around the vial and tied off to the filament contacts, which was a laborious and time-consuming process. Therefore, a new direct insertion probe was developed for rapid introduction of solid samples.
The new probe, illustrated in Figure 4.13, was constructed from a 10.5" length of 1/4" o.d. heavy-wall (4.2 mm i.d.) stainless steel tubing. One end of the tubing was bored out with a .208" drill bit, 2.25" from the end. This end was fashioned into a 1" boat by milling out half of the tubing and a 1/2" notch was also milled out, 1/4" above the boat, for access to the center electrode contact. A stainless steel clip was silver soldered to the top of the tubing over the boat to secure the sample vial. A center electrode for the filament was constructed by flattening one end of a 10.5" length of .060" diameter stainless steel rod in a vice and drilling a 60 gauge hole through the center. A 9.5" length of 3 mm glass tubing was slipped over the rod and the electrode assembly was placed in the center of the probe and sealed at the top with a drop of Varian (Varian Vacuum Products Division, Lexington, MA) Torr Seal epoxy. To heat the sample vial, a filament bed was constructed by running a tantalum wire back and forth across the bottom of a glass insulating boat. This boat was formed from a 2.25" section of 5 mm o.d. glass tubing cut in half and fire-polished along the edges. Once the wire was conformed to fit into the glass, the filament bed was slipped into the probe body and one end of the filament was tied off to the center electrode, while the other end was tied through a 60 gauge hole at the probe tip. A sample vial was slipped into the tip of the probe, and the tension of the clip was adjusted for a secure fit. Sample vials were fashioned from 3/4" sections of 2.6 mm o.d. borosilicate glass tubing sealed at one end. A stainless steel ring with a 6-32 set screw in the side was placed at the top of the probe, to act as a stop.

The custom inlet for the sample probe is shown in Figure 4.14. A plug valve with a 7.2 mm orifice was placed in the center of the inlet which would allow the probe to pass into the ion source and then seal off the vacuum when the probe was removed. The base of the inlet was
Figure 4.13 Diagram of the direct insertion probe used to introduce solid samples into the ion source of the TOF mass spectrometer.
Figure 4.14 Inlet assembly for the direct insertion solid sample probe.
machined from a 3/4" piece of brass roundstock in a similar fashion as the solution inlet, except a 9/32" hole was drilled through the center and a 27/64" hole was drilled into the opposite face, 3/16" deep. To attach the base to the valve, a brass hex nipple fitting (Cajon Co., Macedonia, OH, Cat# B-8-HN-BRT, 9/32" i.d.) was placed in a lathe and one end of the fitting was trimmed down to a tube 27/64" in diameter. Then this end was silver soldered into the 27/64" hole of the base and the assembly was threaded into the bottom of the plug valve. To seal the probe at the top of the inlet, a Cajon Ultra-Torr 1/4" feedthrough fitting was placed at the top of the plug valve. A 1/4" stainless steel tubing side arm was silver soldered into the side of the fitting, to apply rough vacuum to the probe. This side arm was attached to a Circle Seal Co. (Pasadena, CA) plug valve (7.2 mm orifice) and connected to the roughing port with a length of rubber hose. A leak valve (Robbins Aviation Inc.) was placed in the roughing line to regulate the vacuum.

When the probe was placed through the inlet, the stop was adjusted so that the end of the sample vial would be 1/2" above the ion source plates. Current to the probe was furnished from a Hewlett Packard (Palo Alto, CA) Harrison Model 6255A power supply, which was mounted in the rack where the accelerating voltage supply was located.

**System Operating Parameters**

Table 4.1 contains a summary of the typical operating parameters of the hydrogen laser and the mass spectrometer. The optimum voltage settings for the ion optics were determined by examining the width and intensity of an ion peak on the oscilloscope trace while the laser was firing.
Hydrogen Laser

<table>
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<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate voltage</td>
<td>20 kV</td>
</tr>
<tr>
<td>Discharge channel pressure (H₂)</td>
<td>45 torr</td>
</tr>
<tr>
<td>Flowmeter setting</td>
<td>7.5</td>
</tr>
<tr>
<td>Spark gap pressure (N₂)</td>
<td>40-70 psi'</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>

Time-Of-Flight Mass Spectrometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeller plate voltage (V₁)</td>
<td>+45 V</td>
</tr>
<tr>
<td>Accelerating voltage (V₂)</td>
<td>+526 V</td>
</tr>
<tr>
<td>Focusing cylinder voltage</td>
<td>+100 V</td>
</tr>
<tr>
<td>Pickup lens voltage</td>
<td>+330 V</td>
</tr>
<tr>
<td>Detector voltage</td>
<td>-1600 to -1800 V</td>
</tr>
<tr>
<td>Number of spectra averaged</td>
<td>256ᵇ</td>
</tr>
<tr>
<td>Ion source/inlet temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Solid sample probe current</td>
<td>.5-2.5 ampᶜ</td>
</tr>
</tbody>
</table>

ᵇThis value will depend on spacing of the spark gap electrodes.
ᶜTypical value.
ᶜThis value will depend on sample volatility.

Table 4.1 Operating parameters of the hydrogen laser/TOF mass spectrometer system.
Initial experiments with photoactive molecules were designed to examine the important characteristics of the \( H_2 \) laser/TOF mass spectrometer system, such as resolution and sensitivity. Polynuclear aromatic hydrocarbons (PAHs) were studied as the first class of photoactive molecules for three reasons. First, the ionization potentials are well characterized from photoelectron spectroscopy and molecular orbital calculations, which have demonstrated that PAHs of three or more rings have ionization potentials below 7.8 eV\(^9\). Second, many of the PAHs are carcinogenic and the analysis of these species in environmental samples represents an important and complex problem, which can be addressed by the \( H_2 \) laser/TOF approach. Third, resonance-enhanced multiphoton ionization (REMPI) techniques have emphasized the ability to obtain soft, "parents only" ionization of PAHs, therefore, data for single-photon ionization of the hydrogen laser was collected for comparison. Structures of typical PAHs studied are listed in Figure 5.1.

Manipulation of Mass Spectral Data

Rf noise from the laser coupled into the 2-stage preamplifier, giving rise to a "bend" in the baseline of the raw mass spectrum. This effect, shown in Figure 5.2a for a solution injection of acenaphthene in methanol, was severe at high sensitivity. However, when TOF spectra were averaged over many laser pulses, the "bend" was reproducible. Therefore, a custom baseline correction routine was written in ASYST, where the peaks could be masked from the spectrum and then a polynomial fit was made to the resulting baseline, in a series of up to five segments. Once the "fitted" baseline was subtracted, the result (shown
Figure 5.1 Structures of polynuclear aromatic hydrocarbons.
Figure 5.2 Baseline correction of a photoionization mass spectrum for a 10 μl injection of acenaphthene in methanol (1 mg/ml): (a) raw data, (b) corrected spectrum.
in Figure 5.2b) was a flat baseline about 0 V. For a listing of the ASYST baseline correction program, see Appendix C.

Smoothing of mass spectra was attempted using the ASYST function "SMOOTH", which is an algorithm that applies a low pass filter to the data by taking the inverse Fourier transform of a Blackman window response function for an array of data points. The Blackman window response is controlled by a cutoff frequency value for the applied low pass filter, which is limited by the range \(0.5 < f_o < 0.03\), where \(f_o\) is the cutoff frequency in units of cycles/point. For example, an \(f_o\) of 0.25 means that all frequencies with periods shorter than four data points will be eliminated. Application of this algorithm to the TOF waveform data for various \(f_o\) values resulted in a distortion of the mass spectrum, often reducing the intensity of the ion signals. This is attributed to the low sampling frequency of the Tektonix 2430 digital oscilloscope, which yielded a limited number of points across each peak. Therefore, no smoothing was applied to mass spectra presented in this chapter.

**Resolution**

The resolution achievable with the laser/TOF system is demonstrated for the mass spectrum of a solution injection of 4-bromo-N,N-dimethylaniline averaged over 256 laser pulses, shown in Figure 5.3. In this case, the repeller pulse delay was adjusted until optimum resolution of the \(^7\)Br and \(^8\)Br isotope peaks was obtained. The total time-lag between the laser pulse and ejection of the ions from the source was 7.5 \(\mu\)sec (1 \(\mu\)sec delay from the trigger pulse plus 6.5 \(\mu\)sec delay set on the repeller pulse generator). A resolution greater than 100 is possible (50% valley) at a mass of 200. This resolution is comparable to that obtained for 9-bromoanthracene by Lubman and Kronick using a TOF mass spectrometer for REMPI.
Figure 5.3 Photoionization mass spectrum of 4-bromo-N,N-dimethylaniline averaged over 256 laser pulses. Source temperature was 100 °C.
Photoionization Mass Spectra of PAH Solid Residues

Samples of polynuclear aromatic hydrocarbons were purchased from Sigma Chemical Co. (St. Louis, MO) at 98% purity or better and used without further purification. Analytical grade solvents of acetone, ethanol, methanol, and benzene were purchased from EM Science (EM Industries, Gibbstown, NJ) and were used as is except ethanol, which was glass distilled. Stock solutions for most PAHs were made up in an appropriate solvent at a concentration of 1 mg/ml. However, for some of the more insoluble, high molecular weight PAHs, such as tetracene, a more dilute concentration was necessary.

Procedure: To obtain pure PAH mass spectra, a microliter syringe was used to deliver a small volume (typically 10 µl) of a PAH solution into a sample vial, which was placed in a conical centrifuge tube. The tube was heated in a hot water bath to evaporate the solvent at 60 °C under a stream of N₂. The vial was then placed in the tip of the sample probe and analyzed on the laser/TOF system.

Results: Figures 5.4 and 5.5 show photoionization mass spectra of anthracene, pyrene, 1,2,5,6-dibenzanthracene, and benzo[a]pyrene respectively. Each spectrum exhibits a single parent molecular ion peak with no fragmentation. The feature at the beginning of each mass spectra is due to the burst of Rf noise from the laser.

Estimation of Detection Limits For PAHs

Based on solid residue data of a variety of PAHs, detection limits were estimated based on the ratio of the signal height to three times the standard deviation of approximately 100 points of baseline noise from a blank sample. The baseline points were sampled from the mass spectrum in the vicinity of the flight time for the PAH molecular ion. The data for the blank sample was obtained by placing a similar amount of pure solvent into a sample vial, evaporating the solvent at 60 °C under N₂ and obtaining the mass spectrum at the highest possible
Figure 5.4 Photoionization mass spectra of PAH solid residues averaged over 256 laser pulses: (a) anthracene, 10 µg; (b) pyrene, 11 µg.
Figure 5.5 Photoionization mass spectra of PAH solid residues averaged over 256 laser pulses: (a) 1,2,5,6-dibenzanthracene, 10.2 μg; (b) benzo[a]pyrene, 10.1 μg.
sensitivity setting of the oscilloscope, where the baseline noise was on scale. Results for the blank solvent samples were compared to results obtained with no sample in the ion source as well as results from sampling the preamp noise with the laser firing (ion optics off). All three values were very similar, therefore it was concluded that any interfering ion signals, which would arise from background or impurities in the solvent residue, were not observable above the noise level, and that the preamp noise was the limiting factor in determining detection limits. Detection limits for the PAHs are shown in Table 5.1, along with signal to noise values. Sensitivity is in the 30-400 ng range. One advantage of averaging mass spectra over many laser pulses is the ability to reduce the noise level in the spectrum. This effect is demonstrated in Figure 5.6, which shows the graph of the standard deviation of 1024 points of preamp noise averaged over n acquisitions plotted versus the square root of n. The preamp noise data arrays were obtained by sampling the preamp with the digital oscilloscope at a 25 MHz sampling rate.

Photoionization Mass Spectra For Solution Injections of PAHs

For solution injections of PAHs, 10 microliters of a PAH stock solution was injected directly into the heated inlet and the metering valve was opened until the base pressure of the vacuum system fell from 5 X 10⁻⁶ torr to 5 X 10⁻⁷ torr. Mass spectra of perylene and benzo[a]pyrene in benzene solvent are shown in Figure 5.7a and b. When benzene is used as the solvent, a significant solvent peak appears in the spectrum. For the two examples shown in Figure 5.7, the amount (wt/wt) of benzene solvent is over 800 times that of the PAH. Since the ionization potential of benzene is 9.2 eV, the solvent peak arises from e⁻ impact of photogenerated electrons when laser radiation strikes metal surfaces inside the source. A mass of 78 amu was calculated for the benzene solvent peak based on the flight time of this peak and the known
### H2 Laser Photoionization MS Detection Limits for PAHS Based on Signal Height

<table>
<thead>
<tr>
<th></th>
<th>Amount (ug)</th>
<th>Number of Acquisitions</th>
<th>Signal Height (voltage units)</th>
<th>Noise (voltage units)</th>
<th>S/N</th>
<th>LOD at S/N=3 (ng)</th>
</tr>
</thead>
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<tr>
<td>Anthracene</td>
<td>10.1</td>
<td>256</td>
<td>0.328</td>
<td>6.53E-4</td>
<td>502</td>
<td>60</td>
</tr>
<tr>
<td>Benzo[a]Pyrene</td>
<td>10.1</td>
<td>256</td>
<td>0.198</td>
<td>3.98E-4</td>
<td>498</td>
<td>61</td>
</tr>
<tr>
<td>Chrysene</td>
<td>10.1</td>
<td>256</td>
<td>0.0425</td>
<td>3.38E-4</td>
<td>126</td>
<td>241</td>
</tr>
<tr>
<td>1,2,5,6-Dibenzoanthracene</td>
<td>10.2</td>
<td>256</td>
<td>0.174</td>
<td>3.28E-4</td>
<td>530</td>
<td>58</td>
</tr>
<tr>
<td>Tetracene</td>
<td>1.8</td>
<td>128</td>
<td>0.101</td>
<td>1.03E-3</td>
<td>98</td>
<td>55</td>
</tr>
<tr>
<td>Perylene</td>
<td>10.9</td>
<td>256</td>
<td>0.0370</td>
<td>4.38E-4</td>
<td>85</td>
<td>387</td>
</tr>
<tr>
<td>Pyrene</td>
<td>11.0</td>
<td>256</td>
<td>0.896</td>
<td>7.64E-4</td>
<td>1173</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 5.1
Figure 5.6 Plot of standard deviation for data arrays of 1024 points of averaged preamp noise versus the square root of the number of averages. The noise values on the y-axis are in units of voltage.
Figure 5.7 Photoionization mass spectra for solution injections of PAHs averaged over 256 laser pulses: (a) perylene in benzene, (b) benzo[a]pyrene in benzene. Each injection is 10 µl of a 1 mg/ml stock solution.
mass and flight time of the PAH. The formula for this calculation is simply:

\[ m_2 = \left( \frac{t_2}{t_1} \right)^2 m_1 \]  

(1)

where \( m_1 \) and \( t_1 \) are the mass and flight time of the known species (or "mass marker") and \( m_2 \) and \( t_2 \) are the mass and flight time of the unknown species. Broadening of the benzene ion peak can be attributed to the fact that the ions from e\(^{-}\) impact are formed in various regions of the ion source, giving rise to a "space broadening" effect (see Chapter 4) versus the photoionized PAH species, which are always formed in the narrow region defined by the laser beam at the center of the ion source. This effect has been previously discussed by Huth\(^9\).

When the solvent is changed to a species with a smaller cross section such as ethanol or methanol, only a small solvent peak is usually observed above the noise. This is demonstrated in Figure 5.2b foracenaphthene in methanol and in Figure 5.8 for pyrene in ethanol.

For the analysis of PAH mixtures, Figure 5.9a and b show photoionization mass spectra for 10 \( \mu \)l solution injections of five PAHs in acetone. This mixture was prepared by adding 250 \( \mu \)l of each PAH solution (1 mg/mL concentration) to a conical vial, evaporating the solvent at 60 °C under a stream of \( \text{N}_2 \) and then reconstituting the mixture in 300 \( \mu \)l of acetone. The utility of the H\(_2\) laser source is demonstrated for the analysis of PAH mixtures, yielding a simplified spectra with only parent molecular ions for each component. For the mass spectrum in Figure 5.9a, two small solvent peaks appear at flight times of 36 and 32 \( \mu \)sec. These two peaks correspond to ions at mass 58 and 43 which are due to the e\(^{-}\) impact ionization of acetone, yielding the \( \text{M}^+ \) ion and (\( \text{M} - \text{CH}_3 \))\(^+\) fragment ion, respectively.
Figure 5.8 Photoionization mass spectrum for a 10 μl injection of pyrene in ethanol (1 mg/ml) averaged over 256 laser pulses.
Figure 5.9 Photoionization mass spectra of a mixture of five PAHs in an acetone solution: (a) mixture averaged over 128 laser pulses. (b) mixture averaged over 256 laser pulses and displayed on an expanded time scale. A-acenaphthene, N-anthracene, C-chrysene, B-benzo[a]pyrene, D-1,2,5,6-dibenzanthracene.
Conclusions

Photoionization mass spectra of PAHs with the molecular hydrogen laser source gives parent molecular ions with no fragmentation and is therefore a "soft" ionization source, like resonance-enhanced multiphoton ionization with a tunable dye laser. However, mass spectrometry with the H$_2$ laser source is a threshold approach and does not require any changes in wavelength or power to achieve ionization with no fragmentation (see Chapter 2).

Sensitivity of the technique for PAHs was in the range of 30-400 ng, however, the laser source was not the limiting factor. Instead, sensitivity was primarily limited by two factors, the ion detector and noise from the 2-stage preamplifier. For a detector voltage of -1800 V, the ion detector literature claimed a gain of $4 \times 10^7$. To test this value, calculations of the detector gain were made based on the current measured by the preamplifier. Assuming a transmission efficiency of 50%, it was determined that if the gain was indeed $4 \times 10^7$, then the total ion count would only be 4 ions! Assuming a gain of $10^6$, the value rises to 82 ions, which is more reasonable. Therefore, based on these calculations, it was concluded that the gain could be no greater that approximately $10^6$ at the highest voltage setting used. This low gain value makes sense, considering the fact that a 2-stage preamplifier had to be used to amplify the current pulses from the MEM detector. The necessity of using a 2-stage preamplifier creates the problem that any noise from the first stage is subsequently amplified by the second, which results in poor signal-to-noise ratios observed for the PAHs, even when spectra are averaged over 256 laser pulses.

Another problem with the MEM ion detector was distortion of the ion peaks. When the detector voltage was raised from -1600 V to -1800 V, ion peak widths increased by over a factor of 2.
Finally, accurate recording of the ion peaks was limited by the Tektronix 2430 oscilloscope, which could only sample at 25 MHz. Measured mass errors for the PAHs were often a few percent. This could be attributed to uncertainty in defining the peak maxima at the low sampling frequency. As mentioned earlier, the low sampling frequency limited the application of smoothing algorithms to the mass spectra.

At this time, it was concluded that some changes in the time-of-flight system were needed before developing applications of the technique for the analysis of "real world" sample mixtures. These changes, discussed in the next chapter, involved the utilization of improved detector and data acquisition technology, to increase sensitivity and accuracy in recording mass spectra.
In order to improve the sensitivity and mass accuracy of the laser photoionization technique, a number of modifications were made to the time-of-flight mass spectrometer, which are summarized in Figure 6.1. These modifications included a new microchannel plate (MCP) detector, single-stage preamplifier, and 100 MHz data acquisition system. Due to the nature of the detector, the vacuum system was modified with a refrigerated cryobaffle, so that the diffusion pump could be operated for the longer period of time required to pump out the new detector.

The Z-Stack Microchannel Plate Ion Detector

The new microchannel plate detector was a Galileo Electro-Optics Co. (Stubridge, MA) Model FTD-2003 Z-stack detector with three microchannel plates on the front end. This device was custom built at the Galileo Electro-Optics facility.

MCP detectors are known for having excellent characteristics for fast ion pulse measurements. A review of microchannel plate theory, manufacture, and detector applications has been published by Wiza\(^2\). A microchannel plate, shown in Figure 6.2, is an array of 10\(^4\)-10\(^7\) miniature electron multipliers parallel to one another. For the microchannel plates of the Z-stack detector used in this study, each pore was 10 microns in diameter with a 12 micron center-to-center spacing, and a 12° bias angle of the channel axes with respect to the plate face. The channel matrix is fabricated from a lead glass and treated in a manner to optimize secondary emission characteristics of each channel, as well as to make the channel walls semiconducting to allow charge replenishment from an external voltage source. Parallel contact to each channel is provided by vacuum-depositing a thin metallic
Figure 6.1 Diagram of the modified hydrogen laser/TOF mass spectrometer system.
Figure 6.2 Diagram of a microchannel plate (reproduced by permission from Galileo Electro-Optics Co, Sturbridge, MA).
coating, usually Nichrome or Inconel, on the input and output surfaces of the MCP. Resistance across the MCP is on the order of $10^9 \Omega$. A potential of up to 1000 V applied across the MCP produces a bias current flowing through the plate resistance which supplies the electrons necessary to continue the secondary emission process. When an ion strikes the input of the MCP, a cascade of electrons are produced which are accelerated down the channel due to the applied bias, as illustrated in Figure 6.3. A pulse of up to 10,000 electrons can appear at the output and if two or more MCP's are operated in series, a single ion can generate a pulse of up to $10^7$ electrons. This process is demonstrated in Figure 6.4, which shows the operation of a Chevron (dual MCP) ion detector. A comparison of various MCP configurations is illustrated in Figure 6.5.

One problem with ion detectors in mass spectrometry is that many utilize a simple metal plate for a collecting anode. While this scheme is suitable for scanning instruments, time-of-flight involves the measurement of very rapid pulses of ions as they arrive at the detector. Any distortion of the output pulse can significantly degrade resolution. With a metal plate anode, the primary pulse is reflected by the indeterminate impedance of a conducting plane and open conducting wires. These reflections can be nearly the same amplitude as the primary pulse, resulting in severe distortion. One unique characteristic of the Chevron and Z-stack MCP detectors for measurement of ion pulses is the specially designed co-axial anode. This anode is impedance matched to 50 $\Omega$ and mounted on a G-R to BNC connector. The coaxial design has demonstrated the ability to eliminate pulse reflection and subsequent "ringing" of the output pulses associated with a simple metal plate electrode.\textsuperscript{9} The FTD-2003 device is capable of generating pulses approximately 1 nsec wide with a rise time less than 500 psec.

A summary of the characteristics of the FTD-2003 Z-stack detector
Figure 6.3 Ion signal amplification within the pore of a microchannel plate which has been biased at high voltage (reproduced by permission from Galileo Electro-Optics Co., Stubridge, MA).
Figure 6.4 Diagram of a Chevron microchannel plate detector (reproduced by permission from Galileo Electro-Optics Co., Sturbridge, MA).
Figure 6.5 Microchannel plate configurations (reproduced by permission from Galileo Electro-Optics Co., Sturbridge, MA).
is given in Table 6.1. The listed gain and pulse widths were taken from the test data sheet provided with the device. These values were measured for an input pulse of 300 eV electrons. Gain of the device is nearly $10^8$ at normal operating voltages. A comparison of typical operating characteristics for the M-306, Chevron, and FTD-2003 Z-stack detectors are presented in Table 6.2. By using the three MCP configuration, a significant increase in gain is realized without sacrificing pulse resolution.

In order to place the new ion detector inside the flight tube, the tee shaped vacuum housing was disconnected and remounted with the long portion connected to the end of the drift tube and the short portion perpendicular with the tube axis. A blank stainless steel 4" Dependex (Anacon, Burlington, MA) flange was used to construct the detector interface. Three .496" holes were drilled into the flange at the 9, 12, and 3 o'clock positions, and a .748" hole was drilled into the center. Three vacuum MHV connectors (Insulator Seal, Inc., Hayward, CA, part# 9211000) were tig-welded into the smaller holes and a double ended male BNC vacuum feedthrough (Insulator Seal, Inc., part# 9211001) was tig-welded in the center hole. In order to connect high voltage lines to the input and output leads of the MCP stack, lengths of .030" diameter tantalum wire were spot welded to the two leads, and ceramic insulating sleeves were slipped over the wire. The ends of the wire were fastened to beryllium-copper electrical connectors (Insulator Seal, Inc., part# 9924003), which slipped over the posts of the MHV feedthroughs on the vacuum side of the flange. Then the BNC connector of the detector anode was locked in place over the center feedthrough connector. This connector acted as a support post for the detector. A photograph of the flange assembly is shown in Figure 6.6.

Voltage Supplies and Protection Circuit For The MCP Detector

Voltage for the input of the MCP was supplied from a Power Designs
Voltage Across Z-Stack

<table>
<thead>
<tr>
<th>Voltage Across Z-Stack</th>
<th>Gain</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>4.0 \times 10^7</td>
<td>119%</td>
</tr>
<tr>
<td>2300</td>
<td>7.5 \times 10^7</td>
<td>114%</td>
</tr>
<tr>
<td>2400</td>
<td>1.3 \times 10^8</td>
<td>115%</td>
</tr>
</tbody>
</table>

Active Area: 4.9 cm²  
Dark Count: .91 counts/sec/cm²

Pore diameter: 10 microns
Center-to-center spacing: 12 microns
Bias angle: 12°

Table 6.1 Characteristics of the FTD-2003 Z-stack ion detector.
## DETECTOR COMPARISON

<table>
<thead>
<tr>
<th>Type</th>
<th>Maximum Voltage</th>
<th>Gain</th>
<th>Pulse Height Distribution (FWHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-306 magnetic electron multiplier</td>
<td>2000 V</td>
<td>(&lt; 10^6)</td>
<td>---</td>
</tr>
<tr>
<td>Chevron 2 microchannel plates</td>
<td>2000 V</td>
<td>(10^6 - 10^7)</td>
<td>120%</td>
</tr>
<tr>
<td>FTD-2003 Z-stack 3 microchannel plates</td>
<td>3000 V</td>
<td>(5 \times 10^7 - 3 \times 10^8)</td>
<td>110%</td>
</tr>
</tbody>
</table>

*Table 6.2*
Figure 6.6 Photograph of the Z-stack MCP detector and flange mount.
Inc. (Westbury, NY) Model 1570 high voltage DC power supply. For the output of the MCP, a Power Designs Pacific Inc. (Palo Alto, CA) Model HV-1565 DC power supply was used. In order to prevent the MCP stack from being destroyed by ion feedback or electrical breakdown in the event of a vacuum failure, a custom voltage interlock circuit was built. This circuit was designed to monitor the electrometer output of the Veeco RG-81 ionization gauge controller and interrupt power to the detector if the pressure rose above a certain value. The RG-81 controller had a female winchester connector on the back labeled "controller center" with access to the electrometer output, a 21 VAC supply, a +15 VDC and a -15 VDC supply. Therefore, the protection circuit was designed to draw power for the relays and amplifiers from this connector port, which eliminated the need for any other supplies. A schematic diagram of the circuit is given in Figure 6.7. The high voltage lines for the MCP input and output are routed through two separate relays. Current to the relays is regulated by a darlington transistor which is turned on by the output of an operational amplifier. The amplifier is a comparator with the electrometer signal at the noninverting input and a set point voltage from a potentiometer at the inverting input. If the electrometer signal is more positive than the set point voltage, the relays can be activated and will remain on unless the signal falls below the set point voltage. An LED indicator signifies when the vacuum pressure is okay for applying voltage to the detector. Components of the circuit were placed on a breadboard and soldered together. The circuit and relays were mounted inside a 17 1/4" X 8" X 3" aluminum box (LMB, Los Angeles, CA) which was bolted in the center of a 5.25" wide 19" rack panel (LMB, Los Angeles, CA). Holes were drilled in the back of the box for MHV panel feedthrough connectors for the two supplies and a feedthrough for the cable to the RG-81 ionization gauge controller. On the front panel, holes were drilled to
Figure 6.7 Diagram of the vacuum interlock circuit used to protect the MCP detector during operation of the TOF mass spectrometer.
mount the MHV feedthrough connectors (labeled "MCP IN" and "MCP OUT") for the detector voltages, the "VACUUM OKAY" LED indicator, the relay push button, "RELAY ON" indicator light, and the "SET POINT ADJUST" potentiometer. The potentiometer was adjusted so that power to the detector would be interrupted if pressure in the chamber rose above 5 \times 10^4 \text{ torr}. The two power supplies and interlock circuit box were mounted in the rack below the detector housing, where the focusing lens and pick up lens supplies were located.

**Refrigerated Cryobaffle**

In the operating manual of the MCP detector, it was recommended that the detector should be pumped down at high vacuum for a minimum time period of 48 hours before operation. Therefore, the liquid nitrogen cryobaffle on the diffusion pump stack was replaced with a water-cooled cryobaffle which was modified for refrigerated operation. A length of 1" o.d. copper tubing was connected to the input of the cryobaffle which was attached to a type FF-1/4-Z expansion valve (Sporlan Valve Co., St. Louis, MO). The valve was then connected to the high-pressure side of an R-12 (freon) refrigeration cooling unit with a length of 1/4" copper tubing. Another length of 1/4" copper tubing was used to connect the output end of the cryobaffle to the low pressure side of the cooling unit. A type C-032 filter-drier (Sporlan Valve Co.) and sight-window was placed between the expansion valve and the high-pressure service valve of the cooling unit. The sensing bulb of the expansion valve was fastened around the Cu tubing on the suction line just below the cryobaffle output. In order to prevent the system from frost ing up, two layers of Armstrong (Armstrong World Industries, Inc., Lancaster, PA) Armaflex foam insulating tape were wrapped around the copper tubing and expansion valve.

**Detector Preamplifier**

Due to the high gain of the Z-stack MCP detector, a single-stage
preamplifier was sufficient to amplify the current pulses. The circuit of the preamp, based on a single NE5539 high frequency operational amplifier, is shown in Figure 6.8. Components for the circuit were soldered onto a custom built double-sided copper circuit board, which was made using the same procedure outlined in Chapter 4 for the 2-stage preamp. The electrometer circuit was mounted inside a 4" X 2.75" X 2" aluminum BUD box (LMB, Los Angeles, CA) with a female BNC panel feedthrough connector on one end for the input, and a male BNC connector on the other end for the output. A male 9-pin D connector mounted on one side of the box provided +12 V, -12 V, and ground connections to the custom power supply. With a 5.6 kΩ resistor in the feedback loop, the gain was approximately 110. The single-stage electrometer had significantly less noise associated with the output signal than the previous 2-stage device. Response for the electrometer was linear from a few tenths of a microamp up to over 400 microamps, when the device was tested using the procedure described in Chapter 4.

**Improved Data Acquisition System**

The Tektronix 2430 oscilloscope was replaced by a LeCroy (Chesnut Ridge, NY) Model 9400A dual channel digital storage oscilloscope. This device had an analog bandwidth of 175 MHz with a true analog-to-digital sampling frequency of 100 MHz. Buffer memory was 32,000 points per channel and the scope could store up to four waveforms. Data could be transferred to a computer through an address-selectable IEEE-488 port or sent to a plotter directly through an RS-232-C interface. The oscilloscope was equipped with a LeCroy 9400AWFO1 waveform processing firmware package which provided mathematical functions such as averaging, integration, smoothing, and differentiation. For averaging, up to 1 million waveforms could be accumulated.

For acquiring mass spectral data, 10,000 point waveforms were averaged over many laser pulses, stored in buffer memory, and then
Figure 6.8 Circuit diagram of the single-stage preamplifier.
transferred from the oscilloscope to the IBM compatible AT computer for storage and analysis. A set of data acquisition software drivers were written in ASYST for the LeCroy oscilloscope, which are listed in Appendix C. With the new preamplifier, Rf noise from the laser did not present a problem, therefore, baseline correction of the waveforms was unnecessary. Smoothing of mass spectral data was accomplished using the ASYST "SMOOTH" function, which was described in Chapter 5. A cutoff frequency of 0.1 was used in the smoothing algorithm for each waveform data array.

With the larger buffer memory and higher sampling frequency of the new oscilloscope, the complete photoionization mass spectrum could be accurately recorded for a single sample trial. In order to demonstrate the improvement in accuracy obtainable with the LeCroy oscilloscope, a comparison study was performed. In this study, a solid mixture of anthracene and chrysene was analyzed with the mass spectrometer for two separate trials under identical conditions, and the entire mass spectrum was recorded with the Tektronix 2430 and the LeCroy 9400A oscilloscopes. The mass of chrysene was calculated using anthracene as a mass marker for both data sets in order to compare mass accuracies. Results of the experiment are presented in Table 6.3, along with a comparison of sampling frequencies. Greater mass accuracy is achievable with the higher sampling frequency of the 9400A oscilloscope, since the number of points recorded over each peak maxima is increased by a factor of four. Mass accuracies in the 50 ppm range are considered very good for time-of-flight mass analyzers. Another advantage of the higher sampling frequency is the ability to obtain more accurate ion peak area measurements for quantitation.

Optimization of The Modified Mass Spectrometer

A summary of operating parameters for the modified mass spectrometer are shown in Table 6.4. Due to the excellent ion pulse
## MASS ACCURACY COMPARISON

<table>
<thead>
<tr>
<th>Digital Storage Oscilloscope</th>
<th>Maximum Sampling Frequency (MHz)</th>
<th>Time Interval Per Digitized Point (nsec)</th>
<th>Mass Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tektronix Model 2430</td>
<td>25</td>
<td>40</td>
<td>0.14%</td>
</tr>
<tr>
<td>LeCroy Model 9400A</td>
<td>100</td>
<td>10</td>
<td>40 ppm</td>
</tr>
</tbody>
</table>

Measured for chrysene (mw 228.29) with anthracene (mw 178.23) as a mass marker.

Table 6.3 Comparison of photoionization TOF mass accuracy measurements for digital oscilloscopes: Tektronix 2430 versus LeCroy 9400A.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeller plate voltage ($V_p$)</td>
<td>+45 V</td>
</tr>
<tr>
<td>Accelerating voltage ($V_a$)</td>
<td>+636 V</td>
</tr>
<tr>
<td>Focusing cylinder voltage</td>
<td>+100 V</td>
</tr>
<tr>
<td>Pickup lens voltage</td>
<td>+330 V</td>
</tr>
</tbody>
</table>

**MCP Detector Voltages:**
- MCP IN (-HV)                     | -2500 V |
- MCP OUT (Back Plate Bias)        | -200 V  |
- Total voltage across Z-stack     | -2300 V |

**Number of spectra averaged**    | 200-500 |

Table 6.4 Operating parameters of the modified time-of-flight mass spectrometer.
response of the new MCP detector, it was very clear which voltages for the ion optics yielded the best resolution and signal intensity. The repeller plate was operated in a static mode, after discovering that pulsed operation yielded no significant advantage in recording the entire mass spectrum.

In order to determine if there was any benefit in operating the TOF mass spectrometer at a higher accelerating voltage, a study was conducted for the analysis of pyrene. In this study, two sets of accelerating voltages were used which satisfied the focusing condition (see Chapter 4) and the photoionization mass spectrum of pyrene was averaged over 1000 laser pulses. The mass spectrum for the higher accelerating voltage \((V_d + V_r = 2225 \text{ V} \text{ and } V_r = 2000 \text{ V})\), is shown in Figure 6.9a, while the mass spectrum with the lower accelerating voltage \((V_d + V_r = 652 \text{ V} \text{ and } V_r = 607 \text{ V})\) is shown in Figure 6.9b. While the pyrene peak for the lower accelerating voltage is just slightly broader, the peak intensities are the same in each spectrum. In the lower accelerating voltage case, the resolution between the pyrene and background peaks is greater, which is expected, since the ion packets have a longer residence time in the drift tube. Therefore, it was concluded that operating the mass spectrometer at a higher accelerating voltage near 2 kV offered no significant advantage.
Figure 6.9  Photoionization mass spectra for 11 μg of pyrene residue averaged over 1000 laser pulses at two different sets of accelerating voltages: (a) $V_d + V_s = 2225$ V and $V_s = 2000$ V, (b) $V_d + V_s = 652$ V and $V_s = 607$ V
CHAPTER 7
ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS, MIXTURES OF PHOTOACTIVE COMPOUNDS, AND A DRINKING WATER SAMPLE

In this chapter, photoionization mass spectral data is presented which demonstrates how changes in the mass spectrometer system improved sensitivity for analysis. Reproducibility and sensitivity studies are presented for the PAH compounds along with an analysis of mixtures containing pure photoactive components. Finally, the analysis of a drinking water sample for PAH content by the photoionization technique is presented.

Background Mass Spectrum

With enhanced sensitivity of the improved mass spectrometer, background features in the mass spectra were now clearly visible. Figure 7.1 shows the background mass spectrum averaged over 200 laser pulses. The largest features of the background spectrum are the peaks at approximately 22 and 23 microseconds, which correspond to electron impact features of N₂ (28 amu) and O₂ (32 amu) respectively, from air. The peaks in the region from 54 μsec to 80 μsec are probably due to electron impact features from pump oil background. With better focusing of the laser radiation through the ion source, most of the background could probably be eliminated.

Pure PAH Mass Spectra

Procedure and Results: In order to obtain reference mass spectra for pure PAHs, 1 to 3 μl of a solution was added with a microliter syringe to a sample vial, the sample vial was heated lightly with a heat gun to evaporate the solvent, and then the sample vial was placed in the sample probe and analyzed. A filament current of approximately 1 amp was used to heat the vial in the probe. Figures 7.2 through 7.5 show the pure PAH photoionization mass spectra. In each case, the spectrum...
Figure 7.1 Background mass spectrum of the photoionization TOF mass spectrometer, averaged over 200 laser pulses.
Figure 7.2 Photoionization mass spectra of PAHs: (a) anthracene, 3 μg, averaged over 1000 laser pulses; (b) benze[el]acephenanthrylene, 3 μg, 500 laser pulses; (c) benzo[a]pyrene, 3 μg, 1000 laser pulses.
Figure 7.3 Photoionization mass spectra of PAHs averaged over 500 laser pulses: (a) benzo[ghi]perylene, 1 μg; (b) chrysene, 3 μg; (c) coronene, 1.2 μg.
Figure 7.4 Photoionization mass spectra of PAHs averaged over 500 laser pulses: (a) 1,2,3,4-dibenzanthracene, 3 μg; (b) 1,2,5,6-dibenzanthracene, 3 μg; (c) perylene, 1.1 μg.
Figure 7.5 Photoionization mass spectra of PAHs averaged over 500 laser pulses: (a) p-terphenyl, 3.2 μg; (b) pyrene, 3.3 μg; (c) tetracene, 270 ng.
gives a clear parent molecular ion peak for the PAH with small features which matched the background spectrum.

**Reproducibility and Sensitivity Study**

In order to determine how reproducible and sensitive the single-photon ionization technique was for the class of PAH compounds, a study was conducted for a triplicate analysis of each pure component and the background spectrum. PAH $M^+$ signal intensities were measured for each trial using the same procedure outlined in the previous section. The background mass spectrum was also recorded three times and a noise value was estimated by taking the standard deviation of 1000 points in the middle of each background spectrum. Results of the study are presented in Table 7.1. Relative standard deviation is typically a few percent, which is what one would expect given the precision of a 1 to 3 µl injection from a microliter syringe. Obviously, the use of an internal standard would be expected to improve the precision. More importantly, the data indicates that reproducible ion signals are obtainable with averaging, even though the laser radiation varies from pulse to pulse.

Comparing the results of Table 7.1 with Table 5.1, signal to noise ratios of the PAHs improved substantially with the modified system over the old system. In addition, the PAH amounts listed in Table 5.1 are over 3 times more (10-11 µg) than the amounts (1-3 µg) listed in Table 7.1.

Based on the data in Table 7.1, detection limits for each of the PAHs were calculated for a signal to noise ratio of 3. The results are presented in Table 7.2, which indicates that the sensitivity for most PAHs is in the 100-300 pg range. With the modified time-of-flight instrument, detection limits for the PAHs improved by nearly three orders of magnitude, when compared to detection limits listed in Chapter 5 for the previous system. The higher detection limit of $p$-terphenyl is probably due to the fact that this compound has an
<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
<th>Mean Signal (mV)</th>
<th>Std Dev (mV)</th>
<th>%RSD</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthracene</td>
<td>3.03 µg</td>
<td>668</td>
<td>25</td>
<td>3.7</td>
<td>32,100</td>
</tr>
<tr>
<td>benz[e]acephenanthrylene</td>
<td>3.03 µg</td>
<td>338</td>
<td>14</td>
<td>4.2</td>
<td>13,200</td>
</tr>
<tr>
<td>benzo[a]pyrene</td>
<td>3.03 µg</td>
<td>704</td>
<td>19</td>
<td>2.7</td>
<td>33,700</td>
</tr>
<tr>
<td>benzo[ghi]perylene</td>
<td>1.05 µg</td>
<td>248</td>
<td>18</td>
<td>7.2</td>
<td>14,800</td>
</tr>
<tr>
<td>chrysene</td>
<td>3.00 µg</td>
<td>984</td>
<td>38</td>
<td>3.9</td>
<td>13,200</td>
</tr>
<tr>
<td>coronene</td>
<td>1.20 µg</td>
<td>106</td>
<td>3.3</td>
<td>3.1</td>
<td>4,100</td>
</tr>
<tr>
<td>1,2,3,4-dibenzanthracene</td>
<td>3.06 µg</td>
<td>1030</td>
<td>31</td>
<td>3.0</td>
<td>51,300</td>
</tr>
<tr>
<td>1,2,5,6-dibenzanthracene</td>
<td>3.06 µg</td>
<td>1538</td>
<td>59</td>
<td>3.7</td>
<td>60,400</td>
</tr>
<tr>
<td>perylene</td>
<td>1.09 µg</td>
<td>262</td>
<td>16</td>
<td>6.2</td>
<td>10,200</td>
</tr>
<tr>
<td>p-terphenyl</td>
<td>3.18 µg</td>
<td>150</td>
<td>9.9</td>
<td>6.6</td>
<td>7,490</td>
</tr>
<tr>
<td>pyrene</td>
<td>3.30 µg</td>
<td>1262</td>
<td>48</td>
<td>3.8</td>
<td>75,300</td>
</tr>
<tr>
<td>tetracene</td>
<td>270 ng</td>
<td>482</td>
<td>21</td>
<td>4.3</td>
<td>6,460</td>
</tr>
</tbody>
</table>

Three determinations from spectra averaged over 500 laser pulses, except anthracene and benzo[a]pyrene which are averaged over 1000 laser pulses.

Table 7.1 Summary of data from reproducibility study for analysis of PAHs with the improved photoionization TOF mass spectrometer.
# PAH Detection Limits

<table>
<thead>
<tr>
<th>PAH</th>
<th>LOD at S/N = 3 (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthracene</td>
<td>283</td>
</tr>
<tr>
<td>benz[e]acephenanthrylene</td>
<td>690</td>
</tr>
<tr>
<td>benzo[a]pyrene</td>
<td>268</td>
</tr>
<tr>
<td>benzo[ghi]perylene</td>
<td>213</td>
</tr>
<tr>
<td>chrysene</td>
<td>682</td>
</tr>
<tr>
<td>coronene</td>
<td>874</td>
</tr>
<tr>
<td>1,2,3,4-dibenzanthracene</td>
<td>179</td>
</tr>
<tr>
<td>1,2,5,6-dibenzanthracene</td>
<td>151</td>
</tr>
<tr>
<td>perylene</td>
<td>320</td>
</tr>
<tr>
<td>p-terphenyl</td>
<td>1,270</td>
</tr>
<tr>
<td>pyrene</td>
<td>131</td>
</tr>
<tr>
<td>tetracene</td>
<td>125</td>
</tr>
</tbody>
</table>

Table 7.2
ionization potential of 7.8 eV, which is right at the ionization threshold of the laser. This would explain the low photoion signal intensity for p-terphenyl versus the other PAH compounds.

Detection limits for the laser photionization technique are probably determined by two factors. One factor is the sensitivity of the oscilloscope and noise from the analog-to-digital converter (ADC). If waveforms are averaged with the oscilloscope channel input set at ground (GND), the standard deviation of 1000 points is only slightly lower than the standard deviation of noise from the background mass spectrum. Therefore, the majority of the noise is most likely due to the analog-to-digital converter with some contribution from the background. The highest sensitivity of the oscilloscope in the averaging mode is 2 mV/div which corresponds to a full scale of 20 mV. If this scale is divided by 255 increments of the ADC, then the lowest voltage increment is approximately 7.8 X 10^{-5} V, which is about a factor of 2 higher than the typical noise level measured for the background mass spectrum. Therefore, using a more sensitive digitizer with full scale sensitivity in the microvolt range could extend detection limits even lower. It is quite possible that PAH detection limits in the 1-10 pg range, which have been reported for REMPI-TOF, are attainable with the H_2 laser source.

With respect to the ability to obtain higher sensitivity with the H_2 laser/TOF system, two additional factors should also be considered. First, the detector was operated at a relatively conservative voltage of -2300 V across the MCP stack, in order to conserve the detector's lifetime. Second, the laser was operated at a plate voltage of 20 kV for the same reason of preserving the lifetime of the mylar insulation. The detector is capable of operation at higher voltages, which would increase the gain by as much as an order of magnitude. In addition, increasing the laser plate voltage to 25 kV or higher will significantly
increase the energy per pulse, which could increase the photoion yield. It is important to keep in mind that the instrumental system is not completely optimized.

**Mixture Analysis**

In order to demonstrate how the H₂ laser source simplifies mass spectra for mixtures of photoactive compounds, two examples are presented. The first example is a mixture of five polynuclear aromatic hydrocarbons, shown in Figure 7.6, which was obtained by introducing 3 µl of each PAH solution (1 mg/ml) into a sample vial and evaporating the solvent with a heat gun. The resulting solid residue mixture was introduced into the ion source with the sample probe and the mass spectrum was averaged over 500 laser pulses. As expected, the mass spectrum contains only parent molecular ion signals for each component, with no fragmentation. Resolution of the last three PAH ion signals in this case is much improved over the mass spectrum of a similar PAH mixture in Figure 5.9, which was recorded with the previous system.

The second example is a solution mixture of six amines, shown in Figure 7.7. This synthetic mixture was made by mixing 100 µl of each pure amine solution in a small vial and injecting 0.5 µl of the solution into the heated inlet of the mass spectrometer. The mass spectrum clearly contains six parent molecular ion signals for each amine with no fragmentation.

**Analysis of a Drinking Water Sample For PAH Content**

Polynuclear aromatic hydrocarbons in environmental water samples can originate from a variety of sources including petroleum spills, sewage, industrial wastes, and washout from atmospheric pollution. PAH contamination of drinking water can originate from such sources as distribution pipes coated with corrosion-inhibiting coal tar and petroleum-based sealants. The concentration of PAHs in environmental water samples ranges from the ppt (ng/l) to the ppm (mg/l) level so that
Figure 7.6 Photoionization mass spectrum for a mixture of five PAHs averaged over 500 laser pulses: A-anthracene, P-pyrene, C-chrysene, B-benzo[a]pyrene, D-1,2,5,6-dibenzanthracene.
Figure 7.7 Photoionization mass spectrum for a six-component mixture averaged over 500 laser pulses: aniline (m/z 93), triethylamine (m/z 101), N,N-dimethylaniline (m/z 121), tripropylamine (m/z 143), tri-n-butylamine (m/z 185), and trihexylamine (m/z 269). Ion source temperature was 100 °C.
A preconcentration step prior to analysis is almost always required. In addition, PAHs will comprise a fraction of the organic constituents in the complex sample matrix, which often contains many aliphatic, olefinic, and cyclic hydrocarbons as well as simple aromatics, organic acids, esters, and bases. Therefore, analysis of the PAH components will involve a complex sample pretreatment step to isolate and preconcentrate the organic fraction, followed by a chromatographic separation. A comprehensive review of thin layer chromatography, HPLC, and GC methods for the analysis of PAHs in water samples has been published by Futoma et al. This article also includes a review of fractionation and cleanup procedures. One obvious drawback of GC and HPLC techniques is the time required for separation, particularly in the case of higher molecular weight PAHs. For example, elution of benzo[ghi]perylene (mw 276) in HPLC and GC columns can take anywhere from 15 to 45 minutes.

Since the H₂ laser source has a low photoionization threshold, the device should be capable of providing selectivity for the PAHs in environmental water samples containing a variety of organics, with the ability to reduce analysis time by eliminating the need for a GC or HPLC separation step. Therefore, experiments were carried out for the analysis of a drinking water sample for PAH content with the photoionization mass spectrometer. A blank drinking water sample and a sample spiked at the 100 parts-per-trillion level with pyrene, chrysene, benzo[a]pyrene, benzo[ghi]perylene, and coronene were analyzed. A spiked concentration of 100 ppt was chosen as a screening criterion since the World Health Organization's (WHO) maximum permissible limit for PAHs such as benzo[a]pyrene and benzo[ghi]perylene is 200 ppt. The blank drinking water sample was also analyzed by GC/MS.

Experimental

Materials: Analytical grade solvents of isopropanol, methanol,
and hexane were purchased from EM Science (EM Industries, Gibbstown, NJ) and used as is. Bakerbond spe Octadecyl (C₈) 3 ml extraction columns containing 500 mg of solid-phase material were purchased from J.T. Baker Inc. (Phillipsburg, NJ). Extract-clean 4 ml filter columns were purchased from Alltech Associates Inc. (Deerfield, IL) and rinsed with methanol before use. All glassware was rinsed repeatedly with triply-distilled (TDI) water followed by isopropanol.

Sample Collection and Preparation: Drinking water samples were collected at 12 noon from the drinking fountain in the east lobby on the 8th floor of the Gould-Simpson building, located on the University of Arizona campus. The fountain was allowed to run for one minute before the samples were collected. One liter samples were measured in 1000 ml volumetric flasks and the spiked sample was made up by adding a 100 μl aliquot of a methanol solution containing 1 μg/ml of each PAH.

Extraction Procedure: The drinking water sample was divided into two 500 ml portions, 120 ml of isopropanol was added to each portion and the solutions were shaken in plastic bottles. For conditioning and eluting the columns, an Analytichem International (Harbor City, CA) Vac Elut 10-place column aspirator was connected to a liquid trap made from a 2 liter Erlenmeyer flask. The liquid trap, in turn, was attached to a liquid nitrogen cold trap which was connected to a rough vacuum pump. The column was conditioned by passing 3 ml of hexane through the column, drying the column under vacuum for 2 minutes, and then passing 3 ml of MeOH through. 3 ml of TDI water was added and the vacuum was shut off before the liquid level fell below the packing. Then the column was removed from the aspirator and a length of tygon tubing was fastened around the luer tip and connected to the liquid trap. Both portions of the sample were aspirated through the column by carefully submerging the column body in each portion and applying the vacuum. The column was then replaced in the Vac Elut aspirator and rinsed with 10 ml of TDI
water and allowed to dry under vacuum for 5 minutes. A 3 ml portion of hexane was slowly passed through column and collected to elute the PAHs. The hexane portion was then dried by aspirating the solution through a filter column filled with .5 g of MgSO4 and collecting the eluant in a small 4 ml conical reaction vial. To evaporate the hexane, the vial was then placed in a water bath at 60 °C under a stream of N2. The residue was reconstituted in 30 μl of hexane, transferred to a sample vial, and the vial was placed in a conical tube and heated at 60 °C under a stream of N2.

**Photoionization MS Analysis:** The sample vial was placed in the sample probe and analyzed directly. A filament current of 2.0 amps was used and mass spectra were averaged over 200 laser pulses. Two mass spectra were collected during each sample run, the first mass spectrum was collected immediately after the probe filament was activated (from 0-30 seconds) and the second mass spectrum was collected after 30 seconds of heating (from 30-60 seconds).

**GC/MS Analysis:** A drinking water sample was extracted using the procedure listed above, except the residue was reconstituted in 100 μl of hexane and this solution was injected into a gas chromatograph with a quadrupole mass analyzer as a detector. In order to investigate the possibility of organic species arising from the solvent or plastic column body, a blank sample was prepared using the extraction procedure. However, in this case, after the column was conditioned, 20 ml of TDI water was passed though and the column was eluted with hexane and processed in the same manner. The residue was reconstituted in 100 μl of hexane and injected into the GC/MS. Finally, a methanol solution containing the five PAHs at a concentration of 4 μg/μl was analyzed by the GC/MS instrument. GC/MS analysis of the samples with a 70 eV EI source was conducted at the Departmental Mass Spectrometry Facility. Instrumental parameters and chromatographic conditions are listed in
Table 7.3.

Results and Conclusions: The total ion chromatogram for the GC/MS analysis of the blank water sample is shown in Figure 7.8. A total of fourteen peaks appear in the chromatogram and results of a library search for the mass spectrum recorded for each peak is shown in Table 7.4. While the probability of match is low for a few of the compounds, the chromatogram and library search give an idea of the complexity of the drinking water matrix, which contains a variety of organics. Two of the largest peaks in the chromatogram, at retention times of 8.66 and 11.42 minutes, matched the peaks in a chromatogram recorded for the hexane blank column wash. This indicates that the hexane elution of the column probably introduced some impurities from the plastic column body. The library search identified these two compounds as 1,2-benzenedicarboxylic acid, dibutyl ester and 3-nitro-1,2-benzene-dicarboxylic acid, respectively.

The GC/MS analysis did not identify any PAHs in the blank water sample. This however, was not surprising based on the GC/MS analysis of the standard mixture of PAHs. In this case, the chromatogram yielded clear peaks for pyrene and chrysene, but benz[a]pyrene eluted as a broad peak of very low intensity near the end of the chromatographic run. No peaks were observed for benz[ghi]perylene or coronene, therefore, it was concluded that these peaks probably came off the column as very broad peaks and/or were buried in the background. The GC/MS system was producing a high level of background ion signals at the time of the water analysis.

H₂ laser photoionization mass spectra of the blank drinking water sample recorded at two time periods are shown in Figures 7.9a and b, while the two mass spectra recorded for the spiked sample are shown in Figures 7.9c and d. The increase in signal intensity of the peaks in the spiked sample indicates the presence of PAHs benzo[a]pyrene (m/z
Gas Chromatograph:

Hewlett Packard (Palo Alto, CA) Model 5890

Helium carrier gas head pressure: 12.5 psi
Injection port temperature: 250 °C
"Splitless" injection mode
Injection volume: 2 μl
Column temperature program:
  Starting column temperature: 100 °C, time = 1.0 min
  Ending column temperature: 310 °C, time = 5.0 min
  Rate: 20.0 °C/min

Quadrupole Mass Spectrometer:

Hewlett Packard Model 5970 with a RTE-6/VM data system

Source: 70 eV EI
Analyzer temperature: 310 °C
Scan range: 35-600 amu

GC Column:

J&W Scientific DB-1 fused silica capillary
Stationary phase: bonded methyl silicone
Film thickness: 0.40 μm
Internal diameter: 0.18 mm
Length: 20 meters

Table 7.3 GC/MS parameters for drinking water analysis.
Figure 7.8 Total ion chromatogram from the GC/MS analysis of a drinking water sample extracted with a C$_{18}$ precolumn.
### GC/MS Analysis of Tap Water from Drinking Fountain Isolated on C18 Extraction Column

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>Possible Component</th>
<th>MW</th>
<th>% Probability of Match</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.32</td>
<td>2-methyldecane</td>
<td>156</td>
<td>52</td>
</tr>
<tr>
<td>3.70</td>
<td>2,2,5,5-tetramethylhexane</td>
<td>142</td>
<td>54</td>
</tr>
<tr>
<td>4.47</td>
<td>3-methylundecane</td>
<td>170</td>
<td>45</td>
</tr>
<tr>
<td>6.08</td>
<td>2,6-bis(1,1-dimethylethylphenol</td>
<td>220</td>
<td>96</td>
</tr>
<tr>
<td>6.73</td>
<td>hexadecane</td>
<td>226</td>
<td>97</td>
</tr>
<tr>
<td>7.93</td>
<td>octadecane</td>
<td>254</td>
<td>99</td>
</tr>
<tr>
<td>7.98</td>
<td>Isopropyl myristate</td>
<td>270</td>
<td>46</td>
</tr>
<tr>
<td>8.66</td>
<td>1,2-benzenedicarboxylic acid, dibutyl ester</td>
<td>278</td>
<td>91</td>
</tr>
<tr>
<td>9.06</td>
<td>1-methylethyl ester, hexadecanoic acid</td>
<td>298</td>
<td>63</td>
</tr>
<tr>
<td>9.80</td>
<td>docasane</td>
<td>310</td>
<td>76</td>
</tr>
<tr>
<td>10.80</td>
<td>3,7-dimethylnonane</td>
<td>156</td>
<td>62</td>
</tr>
<tr>
<td>11.42</td>
<td>3-nitro-1,2-benzene-dicarboxylic acid</td>
<td>211</td>
<td>89</td>
</tr>
<tr>
<td>12.03</td>
<td>2,6,10,15,19,23-hexamethyl-tetracosane</td>
<td>422</td>
<td>96</td>
</tr>
<tr>
<td>12.80</td>
<td>2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexane</td>
<td>410</td>
<td>97</td>
</tr>
</tbody>
</table>

Table 7.4 Library search results for GC/MS analysis of drinking water sample.
Figure 7.9 Photoionization mass spectra of a blank drinking water extract, (a) and (b), and a spiked drinking water extract, (c) and (d), taken during two heating time intervals of the sample probe. Each spectra was averaged over 200 laser pulses.
benzo[ghi]perylene (m/z 276), and coronene (m/z 300) in the blank sample. For the spiked sample spectra, M⁺ ion signals are clearly identifiable for all five of the PAHs. In addition, the peaks match the flight times of the pure PAH spectra shown in Figures 7.2-7.5. A quantitative estimate of each PAH in the drinking water sample was calculated by measuring the ion peak areas from the blank and spiked spectra for benzo[a]pyrene, benzo[ghi]perylene, and coronene. For measuring the peak areas, the mass spectral data array was converted into an ascii data file in ASYST and imported into a SpectraCalc (Photometrics LTD., Tucson, AZ) data analysis software package. The data array was then smoothed with a 25 point Savitsky-Golay algorithm and the peak areas were integrated. Results of the analysis are presented in Table 7.5.

Analysis of the drinking water sample demonstrates the utility of the photoionization technique. Drinking water samples can be screened for PAH content well below the 100 ppt level without the need for GC or HPLC separation, since other organic species in the sample matrix are not ionized by the laser source. Due to this selectivity, less complex sample pretreatment is necessary, which decreases analysis time and enhances the ability to analyze a larger number of samples. While the technique is not capable of isomer discrimination, it should prove useful for the analysis of PAHs in environmental samples such as airborne particulate matter, water, and soil. In the case of soil analysis, the ability to quickly screen a large number of samples to profile a contaminated area is crucial.
<table>
<thead>
<tr>
<th>PAH</th>
<th>Ion Peak Area from Unspiked Water</th>
<th>Ion Peak Area from Water Spiked at 100 ppt</th>
<th>Concentration (parts-per-trillion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.04544</td>
<td>0.3328</td>
<td>16</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.1087</td>
<td>0.5364</td>
<td>120</td>
</tr>
<tr>
<td>Coronene</td>
<td>0.1087</td>
<td>0.5364</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 7.5 Estimates of PAH content of drinking water sample based on photoionization MS analysis.
CHAPTER 8
PHOTOIONIZATION MS ANALYSIS OF DRUGS OF ABUSE AND PHARMACEUTICALS

In this chapter, the ability of the H₂ laser source to produce soft ionization for drugs of abuse and pharmaceuticals for analytical mass spectrometry is demonstrated. Many drugs of abuse, such as those shown in Figures 8.1 and 8.2, have easy ionizable amine functional groups. The analysis of a pain relief tablet containing codeine is presented, followed by the analysis of urine samples spiked with a variety of commonly abused drugs. Selectivity of the VUV source offers unique advantages for rapid screening of drugs in complex biological matrices such as urine, where samples are analyzed directly after a simple solid-phase extraction procedure. Photoionization mass spectra of some pharmaceuticals are also presented.

Analysis of Codeine in a Pain Relief Tablet

Materials: Analytical reagent grade solvents CH₂Cl₂ and methanol were purchased from EM Science (EM Industries, Gibbstown, NJ) and used as is. The pain relief tablet was a prescription tylenol with codeine #3 tablet, which contains 300 mg of acetaminophen (tylenol) and 30 mg of codeine. The tablet extraction solvent was made by mixing 50 ml of DDI water adjusted to pH 4.0 with phosphoric acid, with 50 ml of methanol.

Procedure: For extraction of the tablet, the procedure given by Sisco et al. was used with some modifications. The pain relief tablet was added to a plastic bottle containing 75 ml of the extraction solvent and the bottle was mechanically shaken for 4 hrs. Afterwards, the mixture was filtered through a .45 μm nylon 66 filter and the filtrate was adjusted to a pH of 9.5 by adding 1 M NaOH dropwise and checking with pH paper. This solution was then extracted twice with two 75 ml portions of CH₂Cl₂ and the organic layers were collected and dried over 2 g of MgSO₄. The solvent was poured through a piece of #1 Whatman
Figure 8.1
<table>
<thead>
<tr>
<th>$R'$</th>
<th>$R$</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>morphine</td>
</tr>
<tr>
<td>COCH$_3$</td>
<td>COCH$_3$</td>
<td>heroin</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>H</td>
<td>codeine</td>
</tr>
</tbody>
</table>

methadone
(Whatman LTD., England) filter paper and collected in the receiving vessel of a Kuderna-Danish evaporative concentrator (part# 6708, Ace Glass Inc., Vineland, NJ) equipped with a Snyder column. The concentrator was heated at 60 °C in a water bath until the solvent volume was ≈4 ml, the Snyder column was replaced with a micro column (part# 6709-07), and then the solvent was evaporated down to 1 ml. After transferring the solvent to a 4 ml conical reaction vial, the solution was evaporated to a residue at 60 °C under a stream of N₂ and then reconstituted in 2 ml of methanol. 5 μl of the methanol solution was placed in a sample vial and heated with a heat gun to evaporate the solvent. Then the vial was placed in the sample probe and analyzed directly in the mass spectrometer. A sample probe filament current of 2 amps was used to heat the sample vial.

Results: The photoionization mass spectrum, shown in Figure B.3, gave a clear M⁺ ion peak for codeine with no fragmentation. All of the smaller peaks were identified as background ion signals. Selectivity of the photoionization source is demonstrated in the analysis of the tablet extract, due to the fact that no signal was observed at a flight time of 51 μsec (m/z 151) for the acetaminophen, even though this compound was present in a ten fold excess over the codeine. Acetaminophen and other amide compounds typically have ionization potentials well above the 7.8 eV threshold of the hydrogen laser source.

Screening of Drugs of Abuse in Urine

In order to appreciate why the photoionization technique offers some unique advantages for drug screening, it is helpful to examine the most commonly-used screening technique, enzyme-multiplied immunoassay (EMIT). An illustration of the EMIT process appears in Figure B.4. Drug-specific antibodies are first added to the specimen. If drug molecules are present, they immediately bind to the antibody sites. Then enzyme-labeled drugs are added to the mixture, which will bind to
Figure 8.3 Photoionization mass spectrum for an extract of a prescription pain relief tablet containing codeine, averaged over 500 laser pulses. The peak at 72 microseconds corresponds to the molecular ion of codeine, m/z 299.
Figure 8.4 Illustration of the enzyme-multiplied immunoassay technique (EMIT) for drug testing of urine samples.
free antibody sites and become enzymatically inactive. An enzyme chromogenic substrate is then added, initially colorless, which turns color upon being converted to a product species by a free enzyme-labeled drug molecule. This color change can be measured with a spectrophotometer. If a low drug concentration of the abused drug is present in the urine specimen, as illustrated to the left of Figure 8.4, then a large concentration of antibodies will be present and most of the enzyme-labeled drug will be bound to antibody sites. As a result, there will be reduced enzyme activity and a very small color change. However, if a large concentration of drug is present, a large portion of the antibody sites will already be occupied by the abused drug in the sample when the free, enzyme-labeled drug is added. Therefore, enzyme activity will result in a deeper color change, which is illustrated to the right of Figure 8.4.

One unique advantage of EMIT is that it is a homogenous technique, where reagents, purchased in a kit form, are added directly to the urine sample without any prior separation or sample pretreatment. Therefore, the test is rapid, simple, easily automated, and requires only a minimal skill level of the operator. In addition, test reagents are relatively inexpensive, therefore cost per sample is low, which is why the technique is widely used in such areas as employment screening. However, the EMIT technique has several disadvantages. The binding of the drug to the antibody is affected by many factors such as urine pH and salt concentration, which can vary from person to person. In addition, these factors can be altered by a person ingesting an adulterate such as vinegar, which will alter urine pH. While the presence of adulterates can be tested for and detected, the person still must be retested at a later date for the abused drug. Another problem with the EMIT technique is cross-reactivity, where some other molecule can mimic the behavior of the abused drug and bind to the antibody.
Cross-reactivity leads to false positive results. Other drugs, such as those found in prescriptions, are known to produce false positives in EMIT. Finally, contamination of the urine sample can produce false negative results. In a drug-testing facility, due to the possibility of a false positive result, every sample that tests positive by EMIT must be confirmed with GC/MS, which increases testing costs due to the time and complexity involved in the analysis (see Chapter 1). The EMIT screen cut-off concentrations for commonly abused drugs in urine are listed in Table 8.1, along with the actual species (parent drug or metabolite) which is detected. These values are taken from product literature of the Syva Company (Palo Alto, CA), which supplies the test reagents for EMIT. Detection times for commonly abused drugs are listed in Table 8.2. The ability to confirm drug use after a period of time is directly dependent on the screen cut-off values (sensitivity) of the EMIT approach as well as the degree of drug use.

Given the disadvantages of EMIT for drug screening, alternate approaches, such as those discussed in Chapter 1 for mass spectrometry, have been developed with the goal of providing rapid analysis with minimal sample pretreatment. In this case, mass analysis of the drug compound provides a higher degree of confidence in confirming identification. However, these techniques often were unable to detect drugs at realistic screening levels due to the nonselective nature of the ion source and complexity of the biological sample matrix. Since the hydrogen laser is a soft ionization source capable of giving parent molecular ions for drugs with selectivity, experiments were carried out to evaluate the system as an alternative for screening abused drugs in urine. Pooled urine samples were spiked with the drugs, and a simple solid-phase extraction procedure was utilized for sample clean up. The resulting extracts were then analyzed directly with the sample probe.

Materials: Methadone, morphine, codeine, phencyclidine (PCP), and
### Screen Cut-off Values For Drugs In Urine By EMIT

<table>
<thead>
<tr>
<th>Drug Class</th>
<th>Drugs Detected</th>
<th>Screen Cut-off (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amphetamines</td>
<td>Amphetamine, methamphetamine</td>
<td>300</td>
</tr>
<tr>
<td>Cocaine</td>
<td>Benzoylecgonine</td>
<td>300</td>
</tr>
<tr>
<td>Methadone</td>
<td>Methadone metabolites</td>
<td>300</td>
</tr>
<tr>
<td>Opiates</td>
<td>Morphine, codeine and other</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>metabolites</td>
<td></td>
</tr>
<tr>
<td>Phencyclidine</td>
<td>Phencyclidine metabolites</td>
<td>75</td>
</tr>
</tbody>
</table>

Source: Business Health Associates, Tucson, AZ
## Detection Times For Drugs In Urine By EMIT

<table>
<thead>
<tr>
<th>Drug</th>
<th>Common Names</th>
<th>Detection Time (light use/chronic use)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amphetamines</td>
<td>Speed, crystal, dexies, ice</td>
<td>1-12 hours</td>
</tr>
<tr>
<td>Cocaine</td>
<td>Crack, snow</td>
<td>1-2 days/4-6 days</td>
</tr>
<tr>
<td>Methadone</td>
<td>Dolophine, etc.</td>
<td>1-4 days</td>
</tr>
<tr>
<td>Opiates</td>
<td>Heroin, codeine, etc.</td>
<td>2-4 days/more than 1 week</td>
</tr>
<tr>
<td>Phencyclidine</td>
<td>PCP, angel dust</td>
<td>2-7 days</td>
</tr>
</tbody>
</table>

Source: Business Health Associates, Tucson, AZ

Table 8.2
cocaine were purchased from Alltech Associates Inc. (Deerfield, IL) as DEA exempt solutions of HCl salts in 1 ml of methanol. The freebase concentration of drug in each solution was 1 mg/ml. Bond Elut Certify solid phase extraction columns with 10 ml reservoirs were purchased from Analytichem International (cat# 29904, Harbor City, CA). A 10 place Analytichem International Vac Elut aspirator unit was used for conditioning the columns and collecting effluents. The Vac Elut aspirator was connected to a vacuum trap as described previously in Chapter 7. Analytical reagent grade solvents of methanol, methylene chloride, isopropanol, and ethyl acetate were purchased from EM Science (EM Industries, Gibbstown, NJ) and used without further purification. Phosphate buffer (0.1 M KH$_2$PO$_4$, pH=6.0), acetate buffer (0.1 M, pH=4.0), 0.1 M acetic acid, and 0.1 M HCl solutions were prepared fresh each month, while eluting solvents CH$_2$Cl$_2$/isopropanol (20:80) with 2% NH$_2$OH, and 2% NH$_2$OH in ethyl acetate, were made fresh each day. Each week, 25 ml urine samples were pooled from seven healthy, male graduate student volunteers and stored in a tightly-sealed plastic bottle kept in the dark at 2 °C. A 5 ml aliquot of the pooled urine sample was transferred into a 15 ml polycarbonate conical centrifuge tube (Nalgene Co., Rochester, NY) and spiked with the drug solution.

**Procedures:** For extraction of the blank and spiked urine samples, the procedures outlined in the Bond Elut Certify instruction manual were used, except the internal standard addition and drug derivatization steps were omitted. The extracts were analyzed directly with the sample probe, using a filament current of 1.0 amps to heat the sample vial. After a heating time of approximately one minute, the parent drug ion peak intensity began to level off at its maximum value and data acquisition was initiated, where each mass spectrum was acquired by signal averaging over 200 laser pulses. A blank urine sample extract was then immediately analyzed in the same manner.
For the extraction procedures listed below, after the last solvent was added in the column conditioning step, the vacuum was interrupted before the solvent level fell below the sorbent bed. Then the urine sample was added to the column, and the vacuum of the Vac Elut aspirator was adjusted so that the sample took a minimum time of 2 minutes to pass through the column.

**Cocaine:** To each urine specimen, 2 ml of phosphate buffer was added, followed by vortexing to mix the solution. The pH of the sample was then checked with pH paper to be between 4 and 6. A Bond Elut Certify column was placed in the aspirator and conditioned with 2 ml of methanol followed by 2 ml of phosphate buffer. The sample was slowly aspirated through the column and the column was rinsed with 3 ml DDI water, 3 ml of 0.1 M HCl, and 9 ml of methanol. A collecting tube was placed in a rack and the rack was placed inside the aspirator. A 2 ml aliquot of CH₂Cl₂/isopropanol (80:20) with 2% NH₄OH was slowly aspirated through the column and collected. The eluting solvent was transferred to a 4 ml conical vial and evaporated in a water bath at 60 °C under a stream of N₂. The residue was reconstituted in 30 μl of eluting solvent and transferred to a sample vial, which was then placed in the bottom of a 15 ml conical tube. The tube was heated in a water bath at 60 °C under N₂ until the solvent in the vial had completely evaporated.

**Opiates:** After 1 ml of 12 M HCl was added to each urine sample, the sample was hydrolyzed in an oil bath at 120 °C for 30 minutes, allowed to cool, and then 1.25 ml of 10 M KOH was added. The pH of the sample was checked with pH paper for a range of 7-8 and the pH was adjusted by dropwise addition of 1 M NaOH if necessary. A column was placed in the top of the Vac Elut apparatus and conditioned with 2 ml of methanol followed by 2 ml of DDI water. Then the urine specimen was aspirated through the column and the column was rinsed sequentially with 2 ml of DDI water, 1 ml of 0.1 M of acetate buffer, and 2 ml of
methanol. The column was dried under vacuum for 2 minutes and then
eluted with a 2 ml aliquot of CH₂Cl₂/isopropanol (80:20) with 2% NH₄OH.
Then the extract was processed for direct analysis using the same
procedure described in the previous section.

Phencyclidine/Methadone: For urine samples spiked with these
drugs, the same extraction procedure listed for cocaine was used with
the following exceptions: For the column rinse step, 1 ml of 1.0 M
acetic acid was added, the column was allowed to dry under vacuum for
five minutes, and 6 ml of methanol was aspirated through. The column
was allowed to dry under vacuum for 2 minutes, and then eluted with a
2 ml portion of 2% NH₄OH in ethyl acetate.

Results: Photo ionization mass spectra for extracts of a urine
blank and urine spiked with 20 ppm cocaine are shown in Figure 8.5a and
b. The spiked sample contained two principal ion peaks of flight times
which corresponded to cocaine molecular ion (m/z 303) and a fragment at
m/z 182 due to loss of benzoate, which is also observed in the EI mass
spectrum of cocaine. However, in this case, the M⁺ peak is the most
intense signal, whereas in EI only a weak parent molecular ion signal is
observed. The urine blank spectrum shows a few peaks due to the matrix,
but these peaks are of low intensity compared to the M⁺ signal of the
sample spiked with cocaine. In comparing the blank and spiked spectra,
there were no significant matrix peaks which interfered with the parent
or fragment ion signals. A molecular ion signal for cocaine was clearly
observable for urine samples spiked at concentrations as low as 500 ppb.

The photoionization/TOF mass spectra for extracts of a urine
blank, urine spiked with 1 ppm codeine, and urine spiked with 400 ppb
morphine and codeine are all shown in Figure 8.6. The spiked urine
samples show clear M⁺ ion peaks with no fragmentation and only a few low
intensity peaks from the matrix background. In this case, the urine
blank spectrum correlated very well with the background signals observed
Figure 8.5 Photoionization mass spectra for (a) urine blank and (b) urine sample spiked with cocaine, analyzed using the Bond Elut extraction procedure for cocaine.
Figure 8.6 Photoionization mass spectra for urine samples processed using the Bond Elut extraction procedure for opiates: (a) urine blank, (b) urine spiked with codeine, (c) urine spiked with both morphine and codeine.
in the spiked samples. Again, there were no significant matrix peaks which would interfere with the parent ion signals at this concentration level. For urine samples spiked with both morphine and codeine as low as the 200 ppb level, each drug gave a clearly identifiable M+ ion peak.

Photoionization mass spectral data of extracts from a urine blank, urine spiked with 1 ppm PCP, and urine spiked with 200 ppb PCP are shown in Figure 8.7. For the spiked samples, an intense molecular ion peak for phencyclidine (m/z 243) was observed with no fragmentation. The identification of the peak at ≈67 μsec in the blank sample is unknown, but if this peak had appeared in the spiked sample, it still would not have interfered with the M+ peak for PCP, which had a flight time of 65 μsec.

For methadone, mass spectra for a blank urine sample, urine spiked with 1 ppm, and urine spiked with 200 ppb are shown in Figure 8.8. A clear parent molecular ion signal with a flight time corresponding to m/z 309 appeared in each sample spiked with methadone. It is unclear why the large ion signal at ≈67 μsec appeared in the blank sample. This signal also appeared in the PCP urine blank, which was extracted by the same procedure. It is possible that this peak could be due to some photoactive species in the urine matrix. Another possibility is that there could be a relatively large amount of some matrix component, such as a urinary aromatic acid, which has a large electron impact cross-section. However, this peak did not interfere with the methadone or PCP molecular ion signal.

After a spiked or blank urine extract was analyzed, the background usually returned to the level that would normally be observed in the source (Figure 7.1, Chapter 7) after approximately a minute, provided the ion source was heated at 100 °C. Given the time involved in running a sample on the TOF instrument, such as time taken to pump out the sample probe and the time period for data acquisition, a sample
Figure 8.7 Photoionization mass spectra for urine samples analyzed using the Bond Elut extraction procedure for phencyclidine/methadone: (a) urine blank, (b) urine spiked with 1 ppm phencyclidine, (c) urine spiked with 200 ppb phencyclidine.
Figure 8.8 Photoionization mass spectra for urine samples analyzed using the Bond Elut extraction procedure for phencyclidine/methadone: (a) urine blank, (b) urine spiked with 1 ppm methadone, (c) urine spiked with 200 ppb methadone.
throughput for the mass analysis step in drug screening is estimated at 3 minutes.

Laser Photoionization Mass Spectra of Pharmaceuticals

In addition to drugs of abuse, the molecular hydrogen laser is capable of producing soft ionization in a variety of pharmaceuticals. Previously, Huth and Denton demonstrated the ability to obtain parent molecular ions with no fragmentation for phenothiazine tranquilizers with the H₂ laser source. In this section, the classes of pharmaceuticals which can be ionized by the VUV photons are extended to a wider range. Photoionization mass spectra are presented for a couple of pain relief agents, nefopam and 4-aminoantipyrine, as well as a tricyclic antidepressant, imipramine, and a cardiovascular drug, verapamil.

Materials: Nefopam hydrochloride, 4-aminoantipyrine, imipramine hydrochloride, and verapamil hydrochloride were all purchased from Aldrich Chemical Company (St. Louis, MO) at 99% purity. Analytical reagent grade solvents of methanol, pentane, methylene chloride, and isoamyl alcohol were purchased from EM Science (EM Industries, Gibbstown, NJ) and were all used without further purification except isoamyl alcohol, which was glass-distilled. Extract-clean 4 ml filter columns were purchased from Alltech Associates Inc. (Deerfield, IL) and rinsed with methanol before use.

Procedures: Solutions of each drug were made up in methanol with a concentration corresponding to 1 mg/ml of the freebase drug. The drug stock solutions were stored at 0 °C in the dark. In order to obtain the freebase form of the hydrochloride salts, an extraction was performed for imipramine, nefopam, and verapamil. Since the 4-aminoantipyrine was already in its freebase form, no extraction was necessary. An extraction solvent of pentane/isoamyl alcohol (20:1) was used for verapamil while methylene chloride was used for nefopam and imipramine.
In order to obtain free base extracts, 1 mL of the drug hydrochloride salt solution was added to a screw-cap vial wrapped in aluminum foil, which contained 2 mL of DDI water. This solution was adjusted to a pH of 9.5 by adding 1 M NaOH dropwise and checking with pH paper. Then 4 mL of the extraction solvent was added to the vial and the mixture was mechanically shaken for 15 minutes. The organic layer was drawn off with a glass micropipet and the extraction was repeated with another 4 mL of organic solvent. After collecting the organic layers, any water was removed by aspirating the organic phase through a filter column containing 2 g of MgSO₄, and collecting the effluent in a 4 mL conical reaction vial. The vial was placed in a water bath at 60 °C and the solvent was evaporated to a residue under a stream of N₂. After the residue was reconstituted in 100 μL of methanol, a 2-4 μL aliquot of this solution was added to a sample vial and the vial was heated with a heat gun to remove the solvent. The resulting solid residue was analyzed directly in the mass spectrometer and each spectrum was obtained by averaging over 200 laser pulses.

Results: The photoionization mass spectra of 4-aminoantipyrine and nefopam are shown in Figure 8.9, while the mass spectra of imipramine and verapamil appear in Figure 8.10. For nefopam, 4-aminoantipyrine, and imipramine, only the parent molecular ion is observed with no fragmentation. All other peaks in these three mass spectra are due to small signals from the background.

In the case of the freebase extract of verapamil (Figure 8.10b), the most intense peak was a fragment ion at a flight time of 73 μsec, which corresponds to a mass of 303 amu. An intense molecular ion peak (m/z 454) also appeared at 89 μsec. The fragment ion is due to loss of mass 151 from the M⁺ ion, which corresponds to a cleavage of the C-C bond adjacent to the nitrogen atom. This αβ cleavage, which results in the loss of a radical species with the charge retained on the fragment.
Figure 8.9 Photoionization mass spectra of pain relief agents averaged over 200 laser pulses: (a) 4-aminoantipyrine; (b) nefopam, free base extract.
Figure 8.10 Photoionization mass spectra of (a) imipramine, a tricyclic antidepressant, and (b) the free base extract of verapamil, a cardiovascular drug. Each spectrum was averaged over 200 laser pulses.
containing the nitrogen atom, accounts for the base peak in electron impact ionization spectra of tertiary amines that are not branched at the α-carbon. In this case, loss of the largest branch from the α-carbon is preferred, leaving the charge on the fragment containing the nitrogen atom whose nonbonding electrons provide resonance stabilization. However, in the case of all the other photoactive amines which have been analyzed with the H₂ laser/TOF system, no fragmentation due to αβ cleavage has been observed. Verapamil is a unique exception that can be explained on the basis of the mechanism illustrated in Figure 8.11. Here, cleavage is favored by the formation of the especially stable benzyl radical which is represented by the resonance structures at the bottom left of Figure 8.11. Delocalization of the odd electron into the ring diffuses the free radical character of the molecule. The resulting resonance-stabilized fragment ion is depicted to the right of Figure 8.11. Future studies should be conducted with other tertiary amines which are substituted with a benzyl or allyl group at the γ-carbon, in order to determine if the αβ cleavage depicted in Figure 8.11 is indeed a fragmentation trend for 7.8 eV photoionization of molecules like verapamil.

Verapamil was the only photoactive compound studied which gave a fragment ion that was of greater intensity than the molecular ion. Furthermore, verapamil and cocaine were the only two cases where fragmentation was observed for H₂ laser photoionization.

**Conclusions**

Mass spectrometry with an H₂ laser source offers some unique advantages for the analysis of pharmaceuticals and drugs of abuse in biological sample matrices such as urine. Due to the low ionization threshold of the laser, samples can be analyzed directly after a simple pretreatment step, without the need for a lengthy GC or LC column separation.
Figure 8.11 Mechanism for the fragmentation of verapamil resulting from 7.8 eV photoionization.
Selectivity of the laser was demonstrated for the screening of abused drugs in urine. After a simple solid-phase extraction step, the photoionization mass spectra gave clear parent molecular ion signals for cocaine, morphine, codeine, methadone, and PCP with no fragmentation except in the case of cocaine, where only one fragment ion was observed. While a few ion peaks of low intensity appeared in the mass spectra from the matrix background, none of the peaks were observed to interfere with the ion signals from the drugs. The solid-phase extraction procedures for most of the drug compounds can be carried out in less than 10 minutes and the technique can be automated. A complete automated workstation for solid-phase extraction compatible with the Analytichem International Bond Elut procedures is available from the Zymark Corporation (Hopkinton, MA).

After processing urine samples with the Bond Elut procedure, the resulting solid extracts contained a considerable amount of yellow crystalline matrix material. Visual inspection of sample vials after the analysis revealed that nearly all of this material was volatilized into the ion source. During the course of the abused drug study, a large number of crude urine extracts were introduced into the TOF instrument over a period of two months. However, background spectra recorded on a daily basis looked exactly like the spectrum in Figure 7.1 (Chapter 7) with no increase in intensity. As a result, there was no need to disassemble and clean the ion source. This is a considerable advantage in maintenance over other methods such as GC/MS, MS/MS and GC/MS/MS which were described in Chapter 1.

In comparing the screen cut-off values given for EMIT in Table 8.1 to the concentrations of drugs in the spiked urine samples, it is obvious that the photoionization technique is capable of screening drugs at much lower concentrations. In addition, mass analysis of the technique provides greater confidence in confirming the presence or
absence of the drug near the screen cut-off levels. One final advantage is that the technique is less subject to the chemical interferences which produce false results in EMIT. While sensitivity of the H₂ laser/TOF system in its current configuration is very good for drug screening, the background could be reduced even further by utilizing a system of optical elements to focus the laser radiation through the ion source, eliminating background from photogenerated electron impact.

In order to determine false positive and false negative rates of the H₂ laser/TOF approach, a blind study should be conducted for a series of spiked urine samples which would also be analyzed by GC/MS. The data base from this study could also be utilized to determine screen cut-off values.

In the case of pharmaceutical analysis, the single-photon ionization technique gives parent molecular ions with no fragmentation in most cases. For pharmalogically active molecules such as imipramine, electron impact ionization at 70 eV gives only a very small M⁺ ion signal with extensive fragmentation. As mentioned earlier in Chapter 2, Lubman et al. observed extensive fragmentation for tricyclic antidepressants such as imipramine with resonance-enhanced multiphoton ionization using a tunable dye laser source⁶.

With the ability to achieve soft ionization for pharmaceuticals in biological samples, the H₂ laser/TOF system could be utilized for pharmacokinetic studies, where the drug concentration is monitored over an extended period of time. Currently, these studies often involve extensive sample pretreatment, followed by a GC or LC separation. With the photoionization technique, samples could be collected and analyzed directly following a simple cleanup step, which would reduce analysis time and allow a larger number of subjects (human or animal) to be studied. For drugs where metabolism leaves the amine functionality intact, metabolites could also be identified and monitored.
While many of the drugs and pharmaceuticals with tertiary amine functionalities were determined to be photoactive, there were some classes of these compounds which did not produce an ion signal. One notable class was the barbiturates. A variety of barbiturates were introduced in the system, but no ion signals for any of the molecules were observed. In addition, pharmaceuticals such as theophylline and diazepam (valium) did not produce ion signals. One common aspect of these compounds is that the amine functionality is adjacent to an electropositive carbonyl group, which raises the ionization potential for electrons of the nonbonding orbital on nitrogen. A principal component of urine, uric acid, which also has this structural similarity, has a vertical ionization potential of 8.55 eV as determined from photoelectron spectroscopy data. In the case of uric acid and the barbiturates, these compounds also contain secondary amine functionalities, with a hydrogen atom instead of an electron-releasing aliphatic group. From studying the compounds ionized by the H₂ laser, as well as examining ionization potentials determined from experimental data such as photoelectron spectroscopy, reasonable predictions can be made about what type of pharmaceuticals will be ionized at the 7.8 eV threshold. Tertiary amines, where -R groups are aliphatic chains or aromatic functionalities, are excellent candidates. The classes of pharmalogically active compounds which fall into this category include drugs of abuse, antihistamines, antidepressants, psychotics, tranquilizers, cardiovascular drugs, pain relief agents, and many others.
APPENDIX A

SYSTEM OPERATING INSTRUCTIONS

Hydrogen Laser

1. Refer to Figure 3.2. Check to make sure the valve on the \( \text{H}_2 \) regulator is closed. Also, make sure the two valves labeled "VACUUM" and "GAS INPUT", located on the front of the laser rack, are closed (be careful not to over-tighten these valves). Plug in the channel rough pump and open the valve on the roughing line attached to the pump.

2. After a few minutes, slowly open the valve labeled "VACUUM" on the rack until the needle of the differential pressure gauge begins to rotate counter-clockwise. Then open this valve all the way. Open the hydrogen tank and adjust the regulator pressure to \( \approx 5 \) psi. Slowly open the valve located at the end of the regulator, then slowly open the valve labeled "GAS INPUT".

3. Adjust the flow of hydrogen into the discharge channel by adjusting the gas input valve until the flowmeter on the rack panel reads \( \approx 7.5 \). Then slowly close the vacuum valve until the differential pressure gauge reads 45 torr. After a few minutes, recheck the pressure and flowmeter settings and readjust the two valves if necessary.

4. Open the ultra-high purity nitrogen cylinder attached to the spark gap line and adjust the pressure on the regulator to \( \approx 50 \) psi. Locate the needle valve at the end of the spark gap gas line, which is fastened to an aluminum sheet bolted on the right end of the diffusion pump stand. A pressure gauge is beside this valve. Open this valve wide open for ten seconds to purge the spark gap, then close the needle valve down until only a slight hiss of flowing gas can be heard.

5. Turn on the 120 V and 230 V power lines by throwing the switches located at the top of the laser rack. Locate the trigger generator front panel towards the top of the rack. The mode switch should be on "AUTO". Adjust the frequency multiplier and fine control knobs to the desired duty cycle (typically 10 Hz). Check to make sure the variac is turned fully counter-clockwise, then turn on the switch labeled "MAIN POWER" followed by the switch labeled "HIGH VOLTAGE".

6. Slowly rotate the variac clockwise until the high voltage meter reads \( \approx 16 \) kV, then immediately turn on the "POWER" switch of the trigger generator. Turn the variac clockwise to the desired plate voltage (typically 19-21 kV). DO NOT EXCEED 25 kV!

7. Observe the discharge channel output and the clicking of the spark gap. Triggering should be reproducible without any misfire. Adjust the UHP \( \text{N}_2 \) regulator pressure to obtain reliable triggering. The range of pressures is typically anywhere from 40-80 psi, depending on the spark gap electrode spacing and plate voltage. DO NOT EXCEED 80 PSI SPARK GAP PRESSURE!

Time-of-Flight Mass Spectrometer

1. Turn on the switch labeled "Rough Pump" on the vacuum controller box located underneath the gate valve to the left of the diffusion pump stand. Slowly open the backing valve on the diffusion pump foreline.
After the pump has been on for a few minutes, turn on the refrigeration unit for the cryobaffle. NEVER RUN THE REFRIGERATED CRYOBAFFLE UNLESS THERE IS A VACUUM ON THE DIFFUSION PUMP FORELINE! Once the cryobaffle is cold, turn on the diffusion pump heater by pressing the button on the vacuum controller box labeled "Diffusion Pump". Allow the pump to heat for 30 minutes. When operating the diffusion pump, check the chilled water supply and make sure there are no scheduled chilled water outages.

2. Close the diffusion pump foreline valve and then slowly open the chamber roughing valve. Apply rough vacuum to the chamber until the pressure on the thermal conductivity gauge reads less than 10 microns. Close the roughing valve to the chamber and then reopen the foreline valve to the diffusion pump. Open the gate valve by turning the lever clockwise from the 6 o'clock position to the 12 o'clock position. The thermal conductivity gauge should fall offscale.

3. Check the vacuum in the chamber by turning on the "POWER" rocker switch of the Veeco ionization gauge controller. Check the calibration on the meter by pressing the "CALIBRATE" button and adjusting the "CALIBRATE" knob until the meter deflects to the 10 position of the red "PER TORR" section of the scale. Activate the "FILAMENT" red rocker switch to turn on the ionization gauge tube filament. After a few minutes, degas the tube by flipping the "DEGAS" switch on and allow the tube to degas for about 3 minutes. Turn off the "DEGAS" switch and then wait about five minutes before reading the meter. At the beginning of the vacuum cycle, the pressure in the chamber should be around 5 x 10^{-3} torr.

4. Activate the heating tape on the chamber by turning the switches of the three autotransformers to the "ON" position. Turn on the temperature controller and adjust the temperature of the ion source to 100 °C. Bake out the system for approximately 12 hours. THE SYSTEM SHOULD BE PUMPED OUT AT HIGH VACUUM FOR A MINIMUM OF 15 HOURS BEFORE OPERATING THE MASS SPECTROMETER.

5. The two high voltage supplies for the MCP ion detector and the vacuum interlock control panel are located in a rack to the left of the instrument. Before turning on the high voltage supplies to the detector, make sure all the voltage knobs are set at 0. Activate the "AC ON" and "HV ON" switches of the two MCP detector HV power supplies. The ionization gauge controller and filament should be activated and the red "VACUUM OK" LED indicator on the panel of the detector interlock controller should be on. The cutoff pressure of the detector interlock controller should be set at 1 x 10^{-3} torr. Activate the relays to the high voltage supplies by pressing the "HV RELAYS ON" button. Slowly increase the voltage on the front of the MCP to -800 V and adjust the voltage supply on the backing plate to -200 V. Then increase the voltage on the front of the MCP to -1000 V. Allow the detector to sit at this voltage for 30 minutes. Then increase the voltage supply on the front of the MCP by -100 V increments every 30 minutes until the supply is at -2000 V. At this point, there will be a voltage of -1500 V across the MCP stack. If voltage to the detector is interrupted due to a sudden pressure increase in the vacuum chamber, then the warm-up procedure should be repeated. However, if the detector has been at high voltage for some time, the voltage can be increased in a shorter time period (3-5 minutes per increment).

6. Activate power supplies for the ion source, focusing cylinder, and pickup lens. Adjust each supply to the proper voltage settings (see Chapter 6).
7. Turn on the power supply of the detector preamp. Turn on the HP 222A trigger pulse generator and the LeCroy 9400A digital oscilloscope. Check the trigger output pulse of the generator, which should be ~4 μsec wide and 5 V in amplitude. Turn on the AT computer and load the ASYST software package and the software drivers for the digital oscilloscope.

8. Open the helium cylinder to the purge tube and adjust the regulator to a pressure of ~1 psi. Open the needle valve on the purge tube all the way and allow gas to flow freely for a few seconds. Then close the valve until only a slight hiss can be heard from the valve.

9. Activate the hydrogen laser and observe the mass spectrum on the oscilloscope at the highest vertical sensitivity and a time base of 10 μsec/div. Adjust the triggering level to achieve reliable triggering of the scope. Then switch the oscilloscope to the "summation averaging" mode. Background ion peaks should be clearly visible. Ions from the background will assist in outgassing the MCPs by "scrubbing" the plates with a small input flux of ions. While the laser is operating, allow the detector to sit at the initial voltage for about 3 minutes and then increase the voltage at the MCP front end by -100 V. Repeat this procedure until the MCP front end voltage is at the desired operating value, ~2500 V (~2300 V across the Z-stack).

10. Introduce the sample into the ion source, using either the heated inlet for solutions or the direct probe for solid residues (see procedure below).

11. To acquire a mass spectrum, observe the ion signals on the oscilloscope screen until they begin to reach their maximum values. Then, while the scope is in the "summation averaging" mode, press the "TRIGGER ZERO" button to initialize the averaging sequence. Once the sequence is over, the mass spectrum can be stored in either of the two memory buffers (C or D), and then transferred to the computer. To conserve lifetime of the laser, the high voltage supply and spark gap trigger generator should only be activated when necessary for acquiring a mass spectrum. Otherwise, the plate voltage should be set at 0 and the power to the spark gap trigger generator should be turned off.

Sample Introduction

Heated Inlet

1. Refer to Figure 4.10. Adjust the inlet/ion source temperature controller until the inlet is at the desired temperature.

2. With the metering valve fully closed, carefully insert the needle of the microliter syringe into the septum so that the needle goes all the way into the inlet.

3. Introduce the sample, withdraw the needle, and then slowly open the metering valve until the pressure rises to approximately 5 X 10^3 torr. After acquiring the mass spectrum, the inlet can be pumped out by slowly opening the metering valve all the way and observing the chamber pressure reading until the value returns to the original base pressure (approximately 5 X 10^4 torr). When opening the valve, be careful not to let the pressure rise above 1 X 10^3 torr.

Solid Sample Probe

1. Refer to Figures 4.13 and 4.14. Place a sample vial into the tip of
the probe and adjust the tension of the clip if necessary.

2. Place the probe through the Cajon fitting at the top of the probe inlet, slide the probe tip 2.5" into the inlet, and tighten the fitting.

3. Open the plug valve on the roughing side arm of the probe inlet. Close the foreline valve of the diffusion pump.

4. Locate the roughing valve for the probe inlet, bolted to the right front corner of the diffusion pump stand. Slowly open this valve and pump out the probe inlet at rough vacuum for about a minute. Close the plug valve on the inlet side arm, immediately open the diffusion pump foreline valve, and immediately open the feedthrough plug valve in the middle of the probe inlet by rotating the lever counterclockwise from the 9 o'clock to the 6 o'clock position.

5. Carefully slide the probe into the inlet with a gentle twisting motion until the stop rests against the top of the inlet. NEVER FORCE THE PROBE INTO THE INLET! Completely close the roughing valve.

6. Attach the positive lead of the current supply to the center electrode of the probe and attach the negative lead to the set screw at the stop. Activate the laser and then turn on the current supply. Adjust the current depending on the volatility of the sample (≈ 1 amp).

7. Once the sample run is over, turn off the current supply and carefully retract the probe (again, with a gently twisting motion) until the tip has passed completely through the middle plug valve (this corresponds to a distance of 5.5" between the top of the inlet and the probe stop). BE CAREFUL NOT THE CLOSE THE VALVE ON THE PROBE TIP! Close the plug valve by rotating the lever clockwise back to the 9 o'clock position. Loosen the Cajon fitting at the top of the inlet and remove the probe. Discard the sample vial.
APPENDIX B
TROUBLESHOOTING

The Hydrogen Laser System

Malfunction of the hydrogen laser source is usually due to a problem associated with the spark gap, trigger circuit, or a breakdown in the mylar insulation.

The Spark Gap Assembly

1. Ablation of the copper button electrode on the bottom Blumlein plate over time results in buildup of sputtered Cu material on surfaces of the spark gap. Every 3 months or so, the spark gap should be disassembled and swabbed with dilute HNO₃, hexane and acetone to remove the dark residue on the inside surfaces. Check the large silicon O-rings (SL70) which form the spark gap seal and replace them if they are cracked or damaged. The teflon disc can be swabbed with dilute HNO₃ to remove residue buildup. The copper button and the spark gap electrode should be removed and polished with Twinkle™ Brand Copper Cleaner (Drackett Products Co., Cincinnati, OH) to remove oxidation, followed by an acetone rinse. The copper button can be unscrewed from the bottom plate by placing the ends of a surgical clamp into the side holes of the button.

To reset the spark gap spacing, follow these steps:
   a. After reassembling the laser, attach one lead of a continuity tester to the plate where the HV cable is connected (inside the laser rack) and the other lead to the electrode sleeve.
   b. Screw the electrode into the spark gap until continuity is established which indicates the top of the electrode is just touching the Cu button. Mark a line on the electrode sleeve which matches the scribe to the left of the brass spark gap block.
   c. Loosen the electrode assembly and rotate the electrode a few turns counter-clockwise (a good starting point is about 5 turns). Attach the electrode to the pulse transformer lead.
   d. Turn on the laser and check for reproducible triggering. Adjust the spark gap spacing and pressure as necessary.

2. Over time a large portion of the Cu button electrode will be sputtered away, resulting in sporadic triggering of the spark gap which cannot be corrected by changing the N₂ pressure or spark gap spacing. If this occurs, replace the Cu button.

3. A crack in the glass capillary of the spark gap electrode (see Figure 3.3) can cause faulty triggering. Inspect the capillary and replace the electrode with a new assembly. A cracked capillary can be replaced by breaking the glass at the epoxy seal and cleaning out the brass sleeve. Then a new capillary (9.5 cm long, 17/64" o.d.) is sealed at the top with a drop of epoxy. Check the O-ring (#110) around the brass electrode sleeve for cracks or wear. Replace if necessary.

The Trigger Generator (See Figure 3.4)

1. Check the 5 and 2 amp fuses on the back of the trigger generator located inside the laser rack. Replace fuses if necessary.

2. Failure in the triggering circuit is most likely due to a
malfunction of the silicon-controlled rectifier or SCR (EGG5531).

Remove the generator from the rack and remove the top perforated aluminum cover. Unsolder the SCR from the circuit and check its operation by placing the leads of a DVM with a diode checker across the anode ("+" lead) and cathode ("-" lead). The DVM should read "open". Then, with the DVM still connected across the SCR, connect the positive lead to the gate. The DVM should now read "closed". Replace the SCR if necessary.

Replacing Mylar Insulation

Breakdown of the mylar insulation will typically occur after about a year of frequent use. One symptom of this problem is an occasional arc which will occur during laser operation. This breakdown will usually be located in the spark gap, but can also take place along the edges of the insulated bottom plate. Upon inspecting the spark gap, if severe burn marks are found in the mylar, then the bottom plate must be rewrapped.

Procedure For Wrapping Bottom Blumlein Plate With Mylar:

1. With the inner laser frame on its side, disassemble the laser by removing the five lucite cross supports. Remove the two top Blumlein plates and the discharge channel from the bottom plate. Locate the point where the HV cable is attached to the plate connector, =3" from the edge of the bottom plate. Cut away any heat shrink or rubber cement and disconnect the HV cable. Remove the bottom plate from the steel box and place it on a large, flat table. Cut away the tape on the back of the plate and completely unwrap the mylar. Be sure to save the teflon disc inserted between the mylar layers. Detach the HV connector. Peel away any tape left on the plate.

2. Inspect the plate for oxidation. If severe oxidation is present, remove the brass spark gap insert, then wash the plate with acetone to remove any clear acrylic paint. Sand the plate with wet #400 sandpaper. Buff the plate with fine steel wool and polish the plate with household metal polish. Rinse the plate with acetone. Use masking tape to mask off the areas where the spark gap insert and cable connector come in contact with the plate. Then spray paint the plate with several coats of clear acrylic. Check the top Blumlein plates for oxidation and apply the same procedure if necessary. Allow the paint to dry overnight. Reinstall the bottom spark gap insert.

3. Obtain a roll of clear mylar, .05" thick, 48" wide (Herculene Drafting film, cat# 193105, Keuffel + Esser Co., Morristown, N.J.). Place the plate on its opposite side. Place strips of double-sided sticky scotch tape across the plate and lay the edge of the mylar roll over the plate as shown in Figure B.1. Make sure that the edges of the mylar roll are parallel with the top edge of the plate.

4. Bring the roll around the plate once making sure that the mylar is tightly bound around the plate. It is critical that the mylar lays evenly on the tape with no bumps or wrinkles. Lay a series of alternating strips of double-sided sticky tape across the backside as illustrated in Figure B.2. and wrap the plate with another mylar layer. Repeat this procedure until the plate is wrapped with four layers of mylar.

5. Refer to Figure B.3. Bring the roll of mylar around the backside of the plate and cut the mylar along the middle of the plate. Place a
Figure B.1
ALTERNATING STRIPS OF DOUBLE-SIDED STICKY TAPE

Figure B.2
Figure B.3
series of short strips of double-sided sticky scotch tape across the plate. Tightly pull the mylar and lay it across the tape. Place strips of regular scotch tape along the edge of the mylar.

6. Refer to Figure B.4. Use a felt tip pen to draw a line 1 cm away from the bottom curved edge of the plate, parallel to the plate edge. Place a thin sheet of aluminum between the mylar layers and the Blumlein plate to protect the plate during the cutting process. Use an X-ACTO knife (Hunt Manufacturing Co., Philadelphia, PA) to cut the mylar along the line. Make a vertical cut in the excess top layers of mylar and spread the layers out. Trim the excess mylar layers into a 5-6 cm flap running along the curved edge of the plate as shown in the illustration.

7. Refer to Figure B.5 and cut the flap into =4 cm wide tabs. Trim the edges of the tabs so that they fit together and tape them down with strips of scotch tape. Be careful not to cut too far into the mylar, the cuts should stop a few mm from edge of the plate. Smaller tabs should be used to seal the more tightly curved edges. Refer to Figure B.6. Do not tape down the tabs near the tapped hole for the HV connector at this time. Place strips of scotch tape along the short edges of the tabs to seal them in place.

8. Repeat steps 3 through 5 to wrap the plate with an additional four layers of mylar.

9. Check the teflon spark gap disc. Clean it with dilute HNO₃ to remove any burn marks. A new disc can be machined from a piece of 2" diameter teflon round stock. The disc is 1/8" thick with a 1" diameter hole cut from the center. O-ring grooves on each side of the disc must be carefully cut to match the grooves on the top and bottom halves of the brass spark gap housing. Insert the teflon disc in between the two sets of mylar wrappings on the front side of the plate as illustrated in Figure B.7.

10. Turn the plate over on its opposite side. Refer to Figure B.8 and follow the procedure in steps 6 and 7, except alternate the tabs so that they cover the seams along the curved edge from the first wrap.

11. Refer to Figure B.9 and draw a line on the top layers of mylar, 1 cm from top edge of the Blumlein plate, in order to cut the mylar and expose the top edge. Again, place a thin sheet of aluminum between the mylar and the plate to protect the plate. Make a vertical cut through the top excess layers of mylar and spread the layers out. Cut the layers of mylar according to the pattern shown in Figure B.9.

12. Now fold the excess mylar into a flap as illustrated in Figure B.10. Then tape the flap down with scotch tape. Placing lead bricks or a heavy object along the top edge of the plate will help secure the flap. BE CAREFUL NOT TO SCRATCH OR CUT THE MYLAR ON THE FRONT SIDE.

13. Refer to Figure B.11 and attach the HV connector as shown. The screw head and connector lug should be on the plate backside. Trim the tabs and tape them in place around the HV cable connector.

14. Flip the plate over on its front side. Move the plate so that its curved edge is hanging off the end of the table. Refer to Figure B.12. Using a spatula, smooth small globs of silicone rubber cement over the seams located along the curved edge of the plate. Be careful in applying rubber cement on the edge, since the top Blumlein plate must lie flat on the mylar insulation. Smooth silicone rubber cement around
5–6 CM

EXPOSED EDGE OF BOTTOM PLATE

Figure B.4
Figure B.5

SCOTCH TAPE

TAB

CUT
Figure B.6
Figure B.7
Figure B.8

ALTERNATING TABS FOR SECOND WRAP
Figure B.9

EXPOSED EDGE OF BOTTOM PLATE

8 CM

9 CM

15 CM

4 CM

1 CM
the base of the HV cable connector and around the top two corners of the insulated plate. Allow the cement to dry overnight.

15. To cut a hole in the mylar for the spark gap, use a 4" length of 1/16" thick, 2" o.d. stainless steel tube which has been sharpened on one edge with a lathe tool. Line up the sharp edge of the pipe over the spark gap and slowly twist the pipe back and forth to cut away the mylar. The mylar discs can be trimmed away using an X-Acto knife with a #28 curved blade.

16. Replace the completed Blumlein plate in the steel laser box. Reconnect the HV supply line to the plate cable, using heat shrink and silicone rubber cement to insulate the connection.

17. Clean any oxidation from the electrode sheets of the discharge channel with steel wool. Reassemble the system and check alignment of the plates, making sure the spark gap seals together properly before replacing the lucite clamps. Carefully tighten the plastic screws which secure the lucite clamps. Insert the spark gap electrode assembly, connect the N₂ purge line and check for leakage. Reset the spark gap spacing as described in the procedure above.

The Time-of-Flight Mass Spectrometer

The Vacuum System

1. A leak in the chamber vacuum will most likely be due to the failure of O-ring seals in the two 3/4" Cajon ultra-torr fittings in the ion source housing. Check the O-ring in each fitting and replace if necessary. High-temperature silicone O-rings should always be used in these fittings.

2. Refrigerated Cryobaffle. Occasionally, the expansion valve of the freon cooling unit may become plugged which results in a malfunction of the compressor in the cooling system. When the valve becomes plugged, the compressor will repeatedly turn on and then immediately shut itself off. To correct this problem, leave the unit on and then open the valve on the high-pressure side of the compressor to release freon. This will put some back pressure on the expansion valve. Also, heat the expansion valve with a heat gun to open it up. Once the unit begins cooling again, refill the system with freon. Attach a can or tank of freon (R-12) to the service valve on the low-pressure side and slowly open the valve port by rotating the stem clockwise a few turns so the valve is about half open. Observe the sight-window on the high-pressure side and bleed in freon until the window chamber is completely full. Close the low pressure service port by rotating the valve stem completely counterclockwise.

Freon leakage in the system can be checked with a Turner (Sycamore, IL) Model LP-1157 halide gas leak detector.

Sample Introduction Systems

1. Solid Sample Probe and Inlet. Malfunction of the probe is usually due to a bad filament connection or broken filament. Check the filament connections to the center electrode and the probe sleeve (see Figure 4.13). Replace the tantalum filament if necessary.

Leakage in the vacuum system during operation of the probe is usually due to failure in the O-ring seals of the probe inlet (see Figure 4.14). O-rings in the two plug valves will become stretched over time and should be replaced on a regular basis. Check the small O-ring
in the top of the 1/4" Cajon Ultra-torr feedthrough fitting and replace it if necessary. Remove the center of the feedthrough plug valve by disconnecting the circular clip on the backside and pulling the center plug out. Remove the three O-rings. Apply a thin coating of high vacuum grease (Dow Corning Co., Midland, MI) to a new set of O-rings and seat them in place before replacing the plug. Check the three O-rings in the plug valve on the roughing side arm and replace them if necessary.

2. Heated Inlet. A leak in the vacuum system while the heated inlet is in use is usually due to a worn septum. Refer to Figure 4.10. Remove the 1/4" swagelock nut containing the septum assembly and replace the septum. Always use a high-temperature silicone septum.

Repeller Supply

Reduction or loss in ion signal is usually due to a dead +45 V battery in the repeller pulse generator. The +45 V battery is checked by attaching a DVM to the BNC output of the repeller pulse generator labeled "accelerating voltage". Use a BNC banana plug adapter at the DVM. Flip the switch located at the left of the generator from the "OFF" position to the right position labeled "constant voltage" and observe the DVM reading. Then place a 10 kΩ resistor across the leads of the BNC banana plug adapter at the DVM and observe the reading. If the battery is good, the voltage should only drop a few volts from +45 V. If a larger voltage drop is observed then the battery must be replaced. This can be accomplished by removing the pulse generator from the rack and removing the outside cover of the generator by taking out the screws fastened around the front end of the cover (marked with arrows).
APPENDIX C

ASYST SOFTWARE Routines

The following is a list of ASYST software routines used for data acquisition in conjunction with the time-of-flight mass spectrometer. Due to the fact that large waveform data arrays caused problems with memory in ASYST, most of the routines were written in separate files so that only the minimum number of routines could be loaded up to conserve memory. In addition, this approach was necessary to make room in the system memory for overlays in ASYST used for data acquisition, storage, and analysis. In each software routine, an ASYST system filename is listed which must be loaded from DOS by entering the filename at the "C:\ASYST" prompt (in the ASYST directory). The system file contains the necessary overlays and memory configuration to run the program in the custom software file. Once the correct ASYST system file has been loaded, the file routines can then be loaded into the system from a floppy disk by typing "LOAD A:FILENAME" at the "OK" prompt. All ASYST system files, custom routine files, and data files are stored on copies of floppy diskettes. Files can also be loaded from directories on hard drive C. However, for the file IO routines, check the software listings for the proper names of directories which must exist on the hard drive for locating data files.

For an explanation of the word definitions in ASYST see "ASYST version 3.0, Module 1-Tutorial, Module 1-Glossaries, Module 2-Analysis, and Module 4-GPIB Tutorial".
ASYST PROGRAM TO CALCULATE FIELD VOLTAGES FOR THE
TIME OF FLIGHT MASS SPECTROMETER BASED ON WILEY AND
MCLAREN SOURCE PARAMETERS, SEE "REV. SCI. INSTRUM.", 1955
THIS PROGRAM IS DESIGNED TO CALCULATE A DISTANCE AT WHICH
IONS IN A TOF MASS SPEC WILL BE FOCUSED FOR A GIVEN SET OF
ION SOURCE PARAMETERS

SYSTEM FILE IS ASYST
ASYST ASCII FILENAME IS TOF.ASC

JEFFREY W. FINCH 9/90

REAL SCALAR DF1
REAL SCALAR DF2
REAL SCALAR VS
REAL SCALAR VD
REAL SCALAR FFDS
REAL SCALAR ED
REAL SCALAR ES
REAL SCALAR KO

COLON DEFINITION TO ACCEPT ION SOURCE PARAMETERS, CALCULATE
THEORETICAL VALUES AND DISPLAY RESULTS ON THE SCREEN

: CALCD
CR CR ." ENTER DISTANCE OF FIRST ION SOURCE FIELD IN CM: "
#INPUT DF1 :=
CR ." ENTER THE VOLTAGE OF THE FIRST PLATE:"
#INPUT VS :=
CR ." ENTER DISTANCE OF SECOND ION SOURCE FIELD IN CM:"
#INPUT DF2 :=
CR ." ENTER THE VOLTAGE OF THE SECOND PLATE:"
#INPUT VD :=
VS VD - DF1 / ES := 
CALCULATE ES, ED
VD DF2 / ED :=

CALCULATE KO
0.635 ES * ED + 0.635 ES * / KO :=

CALCULATE D
KO KO SQRT + 0.635 * INV NEG 1 + 0.635 * KO 1.5 ** * 2 *
FFDS :=
;

COLON DEFINITION TO RUN PROGRAM ITERATIVELY

: ACCEL
BEGIN
CALCD
CR ." CALCULATE AGAIN (Y/N)? "
"INPUT 1 "LEFT
" N" =
UNTIL
CR CR ." FINISHED"
;
This is a data acquisition driver for the Tektronix 2430 digital oscilloscope using a Capital Equipment GPIB board. Required overlays: GPIB Master (GPIB.SOV) and NEC IEEE 488 (GPIBNAT.SOV).

Jeffrey W. Finch 8/89

ASYST system file is ASYSTGPB
Filename is TEK.AQ

The scope's GPIB address must be set to 8 and the encoding (ENCG) under "GPIB SETUP" must be set to "right binary" (RIBIN), before transferring waveforms from the scope. See the Tektronix, Inc. "2430 Instrument Interfacing Guide", 1985 and the "ASYST version 3.0, Module 4-GPIB", 1989.

integer dim[520] array []data.scope \ define array for waveform integer scalar byte.count \ scalar for storing number of bytes sent \ from oscilloscope 7 string header \ define string for CURVE % waveform header

8 gpib.device scope \ define device and assign address []data.scope []gpib.buffer \ data buffer for scope

: tek.aq
send.interface.clear \ seize control of the bus

0 []data.scope :=
scope listener
selected.device.clear " CURV?" gpib.write \ ask oscilloscope for waveform w/o preamble

scope
eos.on ascii % eos.character \ turn eos on and set eos character
me listener
scope talker \ get waveform header delimited by %
eos.off
stack.listen \ get byte count msb
stack.listen \ get byte count lsb
swap 256 * + \ calc byte count
byte.count :=
buffer.listen \ read numeric data into []data.scope array []data.scope

unpack \ since each data point is a byte unpack the data
sub[1, byte.count] \ leave sub array of points on stack ;
DATA SOURCE PROGRAM FOR TEKTRONIX 2430 SCOPE
THIS PROGRAM IS EXECUTED AFTER A WAVEFORM IS STORED IN THE SCOPE IN ORDER TO SELECT THE SOURCE OF THE WAVEFORM DATA BEFORE IT IS TRANSFERRED OVER.
THIS MENU DRIVEN PROGRAM REQUIRES THE FOLLOWING OVERLAYS:
GPIB MASTER (GPIB.SOV), NEC IEEE 488 (GPIBNAT.SOV), AND MENU TOOLS (MENU.SOV).
Tek.AQ DRIVER MUST BE LOADED BEFORE THE PROGRAM WILL RUN.

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ASYST SYSTEM FILE IS ASYSTGPB
FILENAME IS SELECT2.ASC

4 STRING SOURCE
DEFINE COLON DEFINITIONS FOR "DAT SOU:" GPIB WRITE COMMAND

: CH1
" CH1" SOURCE ":="
;
: CH2
" CH2" SOURCE ":="
;
: REF1
" REF1" SOURCE ":="
;
: REF2
" REF2" SOURCE ":="
;
: REF3
" REF3" SOURCE ":="
;
S SOURCE MENU
MENU SOURCE.MENU
NORMAL.DISPLAY
SOURCE.MENU
" SELECT SOURCE OF DATA" MENU.TITLE
MENU.POP.UP
15 45 22 75 MENU.SHAPE
1 15 MENU.COLOR
MENU.NO.STORE
0 1 " ENTER KEY TO CHOOSE ITEM" MENU.ITEM{ NOP }
1 11 " ESC KEY TO LEAVE MENU"
MENU.ITEM{ NOP }
2 1 " CH1" MENU.ITEM{ CH1 }
3 1 " CH2" MENU.ITEM{ CH2 }
4 1 " REF1" MENU.ITEM{ REF1 }
5 1 " REF2" MENU.ITEM{ REF2 }
6 1 " REF3" MENU.ITEM{ REF3 }
MENU.END

PROMPT.SOURCE
STACK.CLEAR
NORMAL.DISPLAY
SOURCE.MENU EXECUTE
NORMAL.DISPLAY
;
\ *************** MAIN PROGRAM ***************

: MAIN.PROGRAM
SEND INTERFACE CLEAR
SCOPE
PROMPT SOURCE
NORMAL DISPLAY
" DAT SOUR:" SOURCE "CAT GPIB.WRITE
TekAQ"
\ THIS IS AN ASYST SET OF COLON DEFINITIONS TO STORE 
\ DATA FROM THE TEK 2430 SCOPE. THIS PROGRAM IS RUN 
\ AFTER THE COLON DEFINITION "MAIN.PROGRAM" HAS BEEN 
\ EXECUTED AND THE WAVEFORM IS READY TO BE STORED IN 
\ A DATA FILE. THE PROGRAM POLLS THE SCOPE AS WELL AS 
\ THE USER FOR INFORMATION ABOUT THE WAVEFORM AND STORES 
\ THIS DATA FOR CONVERTING THE WAVEFORM INTO A TOF 
\ MASS SPECTRUM. 
\ REQUIRED OVERLAYS: FILE IO (DATAFILE.SOV) 
\ TEK.AQ SHOULD BE LOADED INTO THE SYSTEM 
\ JEFFREY W. FINCH 9/89 
\ ASYST SYSTEM FILE IS ASYSTGPB 
\ FILENAME IS FILEINP3.TXT, VERSION 3 OF FILEINPU.TXT 
\ IN THIS VERSION THE DATA FILES WILL BE WRITTEN TO 
\ THE HARD DISK UNDER THE DIRECTORY C:\ASYST\DATA 
\ STRING DEFINITIONS 
30 STRING XFAC 
30 STRING YFAC 
30 STRING XPOS 
30 STRING RPDELAY 
30 STRING DELAY 
20 STRING FILENAME 
\ CREATE FILE TEMPLATE AND DESIGNATE FILENAME 
: CREATE DATA.FILE 
REGULAR DATAFILE 
FILE TEMPLATE 
6 COMMENTS 
INTEGER DIM[ 1025 ] SUBFILE 
END 

CR 
." ENTER NAME OF FILE TO STORE DATA: " 
"INPUT FILENAME ":= \ STORE FILENAME IN STRING 
CHDIR C:\ASYST\DATA \ SWITCH TO DIRECTORY 
C:\ASYST\DATA 
FILENAME DEFER> FILE.CREATE \ SWITCH BACK TO C:\ASYST \ ; 
\ DEFINITION TO WRITE TO DATA FILE 
: WRITE TO FILE 
CHDIR C:\ASYST\DATA \ SWITCH TO C:\ASYST\DATA 
FILENAME DEFER> FILE OPEN 
CR "." ENTER A ONE LINE DESCRIPTION OF DATA" 
CR "." NOT TO EXCEED 64 CHARACTERS" 
CR 
"INPUT 1 >COMMENT 
SEND INTERFACE CLEAR 
SCOPE 
" PATH OFF" GPIB WRITE \ SEND ONLY NUMERICAL DATA 
" WFMPRE? XINC" GPIB WRITE
XFAC GPIB.READ
XFAC 2 >COMMENT
" WFMPRE? YMULT" GPIB.WRITE
XFAC GPIB.READ
XFAC 3 >COMMENT
" WFMPRE? PT.OFF" GPIB.WRITE
XPOS GPIB.READ
XPOS 4 >COMMENT

\ NOW THE PROGRAM WILL ASK THE USER IF THE ION SOURCE REPELLER
\ IS OPERATED IN THE PULSED MODE OR THE STATIC MODE.
\ IN PULSED MODE A DEFAULT VALUE OR ENTERED VALUE CAN BE
\ ACCEPTED AND THIS TEXT VALUE IS SAVED. THE VALUE WILL
\ LATER BE CONVERTED TO A NUMBER AND SUBTRACTED FROM THE
\ TIME WHICH IS DEFINED AS ZERO BY THE SCOPE.
\ IF STATIC MODE IS SELECTED THE SCALAR RPDELAY IS USED TO
\ ACCEPT A VALUE FOR THE DELAY OF A TRIGGER PULSE SENT TO THE
\ SCOPE, THIS VALUE IS MADE NEGATIVE AND STORED SO IT CAN
\ LATER BE 'ADDED' TO THE TIME DEFINED AS ZERO BY THE SCOPE.
CR CR
" IS THE ION SOURCE REPPELLER OPERATED IN A PULSED MODE (Y/N)? 
" "INPUT " Y" "=
IF CR ." ENTER THE REPPELLER PULSE DELAY TIME IN SECONDS 
CR ." (ENTER D FOR DEFAULT OF 1.5E-6 SECONDS): 
" "INPUT "DUP " D" "=
   IF " 1.5E-6 " RPDELAY ":=
   ELSE RPDELAY ":=
   THEN
ELSE CR CR ." ENTER TRIGGER DELAY TIME OF PULSE GENERATOR”
CR ." IN SECONDS (ENTER D FOR DEFAULT OF 0): 
" "INPUT "DUP " D" "=
   IF " 0 " RPDELAY ":=
   ELSE " --" "SWAP "CAT RPDELAY ":=
   THEN
THEN
RPDELAY 5 >COMMENT
CR CR ." DOES THE WAVEFORM HAVE A DELAY TIME FORMAT (Y/N)? 
" "INPUT " N" "=
   IF " 0 " DELAY ":=
   ELSE " DLYTIME? DLY1" GPIB.WRITE
   DELAY GPIB.READ
   THEN
THEN
DELAY 6 >COMMENT
1 SUBFILE SUB[ 1 , 1025 ] ARRAY>FILE
FILE.CLOSE
CHDIR C:\ASYST
\ SWITCH BACK TO C:\ASYST
FILE OUTPUT ROUTINES FOR TEKTRONIX 2430 WAVEFORM DATA

ASYST COLON DEFINITIONS TO READ STORED WAVEFORM DATA
FILE, CONVERT DATA STORED IN COMMENTS TO NUMERICAL
DATA FOR SCALING X AND Y AXES
REQUIRED OVERLAYS: FILE IO (DATAFILE.SOV)
COLON DEFINITIONS FROM FILEINP3.ASC MUST BE LOADED
SINCE COLON DEFINITIONS HERE USE VARIABLES DEFINED IN
FILEINP3.ASC

JEFFREY W. FINCH 9/89
ASYST SYSTEM FILE IS ASYSTGPB
FILENAME IS FILE03.TXT, VERSION 3 OF FILEOUT.TXT
IN THIS VERSION FILES ARE READ FROM THE DIRECTORY
C:ASYST\DATA

DECLARE STRING
64 STRING DATA.TAG

DECLARE SCALARS

INTEGER SCALAR SUBSET
INTEGER SCALAR START
INTEGER SCALAR OFFSET
REAL SCALAR YMULT
REAL SCALAR XINC
REAL SCALAR RPDLT
REAL SCALAR DLT

DEFINE ARRAY TO STORE WAVEFORM
REAL DIM[ 1025 ] ARRAY WAVEFM

DEFINE TOKENS AND ASSIGN THEM TO EXPANDED MEMORY

TOKEN X-AXIS
TOKEN Y-AXIS
EXP.MEM> X-AXIS
EXP.MEM> Y-AXIS

: READ.DATA
-1 6 SCI.FORMAT \ MUST USE THIS FORMAT, OTHERWISE VALUES
\ WILL NOT BE PROPERLY STORED
CR ." ENTER NAME OF WAVEFORM DATA FILE: "
"INPUT FILENAME ":=
CHDIR C:\ASYST\DATA \ SWITCH TO C:\ASYST\DATA FILENAME
DEFER> FILE.OPEN \ OPEN FILE

1 COMMENT> DATA.TAG ":="
2 COMMENT> XFACE ":="
3 COMMENT> YFACE ":="
4 COMMENT> XPOS ":="
5 COMMENT> RPDELAY ":="
6 COMMENT> DELAY ":="
1 SUBFILE WAVEM FILE>ARRAY
FILE.CLOSE
CHDIR C:\ASYST \ SWITCH BACK TO C:\ASYST ROOT DIR
;

COLON DEFINITION TO GIVE DATA DESCRIPTION
READ.OUT
CR ..

DESCRIPTION OF WAVEFORM DATA:
CR DATA.TAG "TYPE
CR .." TIME INCREMENT PER POINT IN SECONDS: " XFAC "TYPE
CR .." VOLTAGE PER DIGITIZER LEVEL: " YFAC "TYPE
CR .." TRIGGER POSITION: " XPOS "TYPE
CR .." REPELLER PULSE DELAY TIME: " RPDELAY "TYPE
CR .." SCOPE DELAY TIME: " DELAY "TYPE
; COLON DEFINITION TO SCALE X AND Y AXIS FOR
\ PLOTTING MASS SPECTRUM

; SCALE.XY
\ CONVERT STRINGS TO NUMBERS
XFAC 32 "NUMBER XINC :=
YFAC 32 "NUMBER YMULT :=
XPOS 32 "NUMBER START :=
RPDELAY 32 "NUMBER RPDLT :=
DELAY 32 "NUMBER DLT :=

1024 BYTE.COUNT := \ ASSIGN 1024 PT WAVEFORMS
\ AND DROP CHECKSUM
CR CR .." DO YOU WANT ANY PRETRIGGER POINTS DISPLAYED (Y/N) ? "
"INPUT " Y "=
IF CR .." ENTER THE NUMBER OF PRETRIGGER POINTS "
CR .." (PRESS ENTER FOR DEFAULT OF 20 POINTS): "
#INPUT
IF OFFSET :=
ELSE 20 OFFSET :=
THEN
ELSE 0 OFFSET :=
THEN
\ COMPUTE NEW STARTING TIME FOR X AXIS
START OFFSET - START := \ COMPUTE NEW STARTING POINT
DLT RPDLT - OFFSET XINC * - DLT := \ COMPUTE NEW OFFSET TO
\ SET NEW STARTING TIME IN
\ SPECTRUM FOR X AXIS,
\ INCLUDING THE REPELLER
\ DELAY TIME
\ COMPUTE SUBSET OF DATA POINTS TO START AT TRIGGER POSITION
BYTE.COUNT START - SUBSET :=
\ CREATE X ARRAY
SUBSET REAL RAMP BECOMES> X-AXIS \ CREATE X ARRAY, ASSIGN IT TO
\ TOKEN
X-AXIS XINC * DLT + BECOMES> X-AXIS \ SCALE X AXIS
WAVEFM YMULT *
SUB[ START , SUBSET ] BECOMES> Y-AXIS
;
****** MAIN PROGRAM COLON DEFINITION ******
: OUTPUT
READ.DATA
READ.OUT
SCALE.XY
X-AXIS Y-AXIS
XX.AUTO.PLOT
;
ASYST BASELINE CORRECTION ROUTINE

THIS PROGRAM WILL READ WAVEFORM DATA FILES TAKEN
WITH THE TEKTRONIX 2430 SCOPE FROM DISK AND
APPLY A BASELINE CORRECTION TO THOSE FILES.

THIS PROGRAM USES VARIABLES DEFINED IN THE
FILEINPUT3.ASC FILE AND COLON DEFINITIONS FROM
THE FILE03.ASC FILE. THE VARIABLES AND COLON
DEFINITIONS MUST BE RESIDENT BEFORE THE PROGRAM
WILL RUN. THE SYSTEM FILE MUST CONTAIN THE
FOLLOWING OVERLAYS: WAVEFORM ANALYSIS (WAVEOPS.SOV,
POLY.SOV, AND SPFN.SOV), AND FILE IO (DATAFILE.SOV).

JEFFREY W. FINCH

1990

ASYST SYSTEM FILE IS ASYSTANS
FILENAME IS BASELN.ASC

TYPE COLON DEFINITION "BASE.CORRECT" TO LOAD PROGRAM

VARIABLES

INTEGER SCALAR X1  REAL SCALAR SLOPE
INTEGER SCALAR X2  REAL SCALAR YINT
REAL SCALAR Y1  INTEGER SCALAR SP
REAL SCALAR Y2  INTEGER SCALAR #SEG
INTEGER SCALAR INCRMT  INTEGER SCALAR STP

ARRAYS

DIM[ 24 ] REAL ARRAY MSK.PTS

TOKENS

TOKEN YNEW EXP.MEM> YNEW
TOKEN PART EXP.MEM> PART

COLON DEFINITIONS

: SET.GRAPHICS
ARRAY.READOUT
MSK.PTS READOUT>ARRAY
NORMAL.COORDS
.5 .975 READOUT>POSITION
WORLD.COORDS
CR :" MASK PEAKS IN SPECTRUM"
CR :" BY MOVING CURSOR FROM"
CR :" LEFT TO RIGHT AND SELECT"
CR :" TWO POINTS ACROSS EACH "
CR :" PEAK BY PRESSING THE "
CR :" <HOME> KEY. RESUME PROGRAM"
CR :" BY TYPING 'CONTINUE' AT THE"
CR :" 'OK' PROMPT "
CR :

: MASK.PTS
1 SP :=
BEGIN
UNTIL CHKSEGS
BEGIN
MSK.PTS [ SP ] X1 :=
MSK.PTS [ SP 1 + ] Y1 :=
MSK.PTS [ SP 2 + ] X2 :=
MSK.PTS [ SP 3 + ] Y2 :=
Y2 Y1 - X2 X1 - / SLOPE :=
Y1 SLOPE X1 * - YINT :=
X2 X1 DO I SLOPE * YINT + YNEW [ I ] := LOOP
SP 4 + SP :=
SP #READOUTS 2 * >
UNTIL
;
: CHKSEGS
BEGIN
CR CR ." ENTER THE NUMBER OF SEGMENTS TO FIT"
CR ." THE BASELINE WITH (1-5): 
#INPUT #SEG :=
?DROP \ DROP LOGIC VALUE CREATED
\ FROM INPUT
#SEG 5 > #SEG 1 < OR
WHILE CR ." NUMBER OUT OF RANGE, REENTER: 
REPEAT
;
: CHKINC
BEGIN
CR CR ." ENTER THE NUMBER OF POINTS PER SEGMENT"
CR ." FOR BASELINE FIT (50-200): 
#INPUT INCRMT :=
?DROP
INCRMT 200 > INCRMT 50 < OR
WHILE CR ." NUMBER OUT OF RANGE, REENTER: 
REPEAT
;
: TEST.RANGE
BEGIN
CR CR ." THERE ARE " SUBSET . ." POINTS IN THE "
CR ." DISPLAYED SPECTRUM"
CHKSEGS
CHKINC
SUBSET #SEG INCRMT * <
IF CR CR ." THE NUMBER OF SEGMENTS AND POINTS PER"
CR ." SEGMENT PRODUCT EXCEEDS THE ACTUAL NUMBER OF"
CR ." POINTS IN THE DATA ARRAY, ENTER NEW VALUES:"
FALSE
ELSE SUBSET #SEG INCRMT * - INCRMT >
IF CR CR ." THE NUMBER OF SEGMENTS AND POINTS PER"
CR ." SEGMENT SELECTED DOES NOT COVER THE RANGE OF"
CR ." DATA POINTS, ENTER NEW VALUES:"
FALSE
ELSE TRUE
THEN
UNTIL
CR CR ." THE DATA ARRAY OF " SUBSET . ." POINTS WILL BE FITTED"
CR ." WITH " #SEG . ." SEGMENTS OF " INCRMT . ." POINTS WITH AN"
CR ." ADDITIONAL LEFT-OVER SEGMENT OF " SUBSET #SEG INCRMT * - .
CR ." POINTS."
;
: FIT
 1 STP :=
BEGIN
  STACK.CLEAR
  INCRMT REAL RAMP
  DUP
  YNEW SUB[ STP , INCRMT ]
  5 LEASTSQ.POLY.FIT
  POLY[X]
  BECOMES> PART
  STP INCRMT + STP DO
    PART [ I 1 + STP - ] YNEW [ I ] := LOOP
  STP INCRMT + STP :=
  STP INCRMT + SUBSET >
UNTIL
  STACK.CLEAR
  SUBSET 1 + STP - REAL RAMP
  DUP
  YNEW SUB[ STP , SUBSET 1 + STP - ]
  5 LEASTSQ.POLY.FIT
  POLY[X]
  BECOMES> PART
  SUBSET 1 + STP DO
    PART [ I 1 + STP - ] YNEW [ I ] := LOOP
;
\ *************** MAIN PROGRAM COLON DEFINITION ***************

: BASE.CORRECT
READ.DATA
SCALE.XY
Y-AXIS BECOMES> YNEW
YNEW Y.AUTO.PLOT
SET.GRAPHICS
;

: CONTINUE
MASK.PTS
TEST.RANGE
FIT
Y-AXIS YNEW - BECOMES> YNEW \ ASSIGN CORRECTED ARRAY INTO
\ ASSIGN CORRECTED ARRAY INTO
X-AXIS
YNEW
XY.AUTO.PLOT
;
ASYST DATA ACQUISITION DRIVER FOR
THE LECROY 9400A DIGITAL OSCILLOSCOPE
USING A CAPITAL EQUIPMENT PC-488 CARD

THIS DRIVER CONTAINS COLON DEFINITIONS TO READ IN
THE WAVEFORM DESCRIPTOR AND WAVEFORM DATA AND STORE
THE INFORMATION ON DISK. THE WAVEFORM DATA IS READ
IN AND STORED IN SUBFILE BLOCKS OF 1000 POINTS.
THEN THE DATA CAN BE RETRIEVED FROM THE HARD DRIVE,
THE WAVEFORM DESCRIPTOR INFORMATION IS DECODED, AND
THE DATA ARRAY IS CONVERTED INTO A TIME-OF-FLIGHT
MASS SPECTRUM WHICH IS PLOTTED ON THE SCREEN.

FOR DESCRIPTIONS OF THE CODE SEE THE ASYST VERSION 3.0
MANUALS

FOR PROGRAMMING THE 9400A VIA THE GPIB, SEE SECTION 7
OF THE LECROY 9400A OPERATOR'S MANUAL, JUNE 1989

THE GPIB ADDRESS SETTING ON THE BACK OF THE 9400A
SHOULD BE SET TO 4

REQUIRED OVERLAYS: FILE IO (DATAFILES.SOV), GPIB MASTER
(GPIB.SOV), AND NEC IEEE 488 (GPIBNAT.SOV).

VERSION 3

JEFFREY W. FINCH 9/17/90 REVISED: 11/08/90

ASYST SYSTEM FILE IS ASYSTALT
FILENAME IS 9400DRV.ASC

10 STRING SOURCE
20 STRING FILENAME
20 STRING TOFFSET

*************** NOTE ***************
THE DATA SOURCE FOR TRANSFERRING WAVEFORMS FROM THE SCOPE
IS SET TO A DEFAULT OF "MEMORY C", SINCE THE MASS
SPECTRAL DATA IS USUALLY STORED IN A MEMORY ALLOCATION
OF THE SCOPE AFTER ACQUISITION. THIS CAN BE CHANGED, FOR
EXAMPLE, TO CHANNEL 1, BY TYPING " CH1" SOURCE ":=

" MC" SOURCE ":=

4 GPIB.DEVICE DS01 \ 9400A ADDRESS IS 4
INTEGER SCALAR BYTE.COUNT
INTEGER SCALAR OFFSET
INTEGER SCALAR #PTS := 10000 #PTS :=
INTEGER SCALAR VGAIN
INTEGER SCALAR BPT
INTEGER SCALAR BLKSZ := 1000 BLKSZ :=
INTEGER SCALAR SA :=
INTEGER SCALAR #SWPS
INTEGER SCALAR RANGE := 256 RANGE :=
INTEGER SCALAR ORIGN :=
REAL SCALAR FGAIN
REAL SCALAR DLYTM
REAL SCALAR T/D
REAL SCALAR SMPINT
INTEGER DIM[ 100 ] ARRAY DESCR
INTEGER DIM[ 510 ] ARRAY WAVE

\\ *************** TOKENS ***************
TOKEN XTB EXP.MEM> XTB
TOKEN FDES EXP.MEM> FDES
TOKEN SMSCALE EXP.MEM> SMSCALE
TOKEN BLK1 EXP.MEM> BLK1
TOKEN BLK2 EXP.MEM> BLK2
TOKEN BLK3 EXP.MEM> BLK3
TOKEN BLK4 EXP.MEM> BLK4
TOKEN BLK5 EXP.MEM> BLK5
TOKEN BLK6 EXP.MEM> BLK6
TOKEN BLK7 EXP.MEM> BLK7
TOKEN BLK8 EXP.MEM> BLK8
TOKEN BLK9 EXP.MEM> BLK9
TOKEN BLK10 EXP.MEM> BLK10
TOKEN BLK11 EXP.MEM> BLK11
TOKEN BLK12 EXP.MEM> BLK12

\ COLON DEFINITION TO GET WAVEFORM DESCRIPTOR

: GET.DES
SEND. INTERFACE.CLEAR
DESCR [ ] GPIB.BUFFER
ME TALKER DS01 LISTENER
" RD," SOURCE " .DE" "CAT "CAT GPIB.WRITE
200 MSEC.DELAY \ POLL SCOPE FOR
ME LISTENER DS01 TALKER
BUFFER.LISTEN
UNLISTEN
DESCR UNPACK SUB[ 5, 150 ] BECOMES> FDES \ UNPACK INTO BYTES
\ SKIP THE HEADER
\ AND BYTE COUNT
\ STORE IN TOKEN FDES
;

\ COLON DEF TO CALCULATE THE THREE FACTORS FOR CONVERTING THE
\ INTEGER DATA POINTS INTO VOLTAGE VALUES

: VCALC
FDES [ 1 ]
CASE
22 OF 5.0E-3 FGAIN := ENDOF \ 5 mV
23 OF 10.0E-3 FGAIN := ENDOF \ 10 mV
24 OF 20.0E-3 FGAIN := ENDOF \ 20 mV
25 OF 0.050 FGAIN := ENDOF \ 50 mV
26 OF 0.100 FGAIN := ENDOF \ .1 V
27 OF 0.200 FGAIN := ENDOF \ .2 V
28 OF 0.500 FGAIN := ENDOF \ .5 V
29 OF 1.00 FGAIN := ENDOF \ 1 V
30 OF 2.00 FGAIN := ENDOF \ 2 V
31 OF 5.00 FGAIN := ENDOF \ 5 V
ENDCASE

FDES [ 2 ] VGAIN := \ GET THE VERTICAL GAIN
\ OFFSET VALUE
;

\ COLON DEFINITION TO DETERMINE TIME/DIV
\ FROM WAVEFORM DESCRIPTOR

: TIME.DIV
-1 4 SCI.FORMAT
CASE
FDES[10]

\ 10TH ELEMENT OF DESCRIPTOR

4 OF 2.00E-9 T/D := ENDOF \ 2 NSEC/DIV
5 OF 5.00E-9 T/D := ENDOF \ 5 NSEC/DIV
6 OF 10.0E-9 T/D := ENDOF \ 10 NSEC/DIV
7 OF 20.0E-9 T/D := ENDOF \ 20 NSEC/DIV
8 OF 50.0E-9 T/D := ENDOF \ 50 NSEC/DIV
9 OF 0.100E-6 T/D := ENDOF \ .1 USEC/DIV
10 OF 0.200E-6 T/D := ENDOF \ .2 USEC/DIV
11 OF 0.500E-6 T/D := ENDOF \ .5 USEC/DIV
12 OF 1.00E-6 T/D := ENDOF \ 1 USEC/DIV
13 OF 2.00E-6 T/D := ENDOF \ 2 USEC/DIV
14 OF 5.00E-6 T/D := ENDOF \ 5 USEC/DIV
15 OF 10.0E-6 T/D := ENDOF \ 10 USEC/DIV
16 OF 20.0E-6 T/D := ENDOF \ 20 USEC/DIV
17 OF 50.0E-6 T/D := ENDOF \ 50 USEC/DIV
18 OF 0.100E-3 T/D := ENDOF \ .1 MSEC/DIV
19 OF 0.200E-3 T/D := ENDOF \ .2 MSEC/DIV
20 OF 0.500E-3 T/D := ENDOF \ .5 MSEC/DIV
21 OF 1.00E-3 T/D := ENDOF \ 1 MSEC/DIV
22 OF 2.00E-3 T/D := ENDOF \ 2 MSEC/DIV
23 OF 5.00E-3 T/D := ENDOF \ 5 MSEC/DIV
24 OF 10.0E-3 T/D := ENDOF \ 10 MSEC/DIV
25 OF 20.0E-3 T/D := ENDOF \ 20 MSEC/DIV
26 OF 50.0E-3 T/D := ENDOF \ 50 MSEC/DIV
27 OF 0.100E-3 T/D := ENDOF \ .1 SEC/DIV
28 OF 0.200E-3 T/D := ENDOF \ .2 SEC/DIV
29 OF 0.500E-3 T/D := ENDOF \ .5 SEC/DIV
30 OF 1.00E-3 T/D := ENDOF \ 1 SEC/DIV
31 OF 2.00E-3 T/D := ENDOF \ 2 SEC/DIV
32 OF 5.00E-3 T/D := ENDOF \ 5 SEC/DIV
33 OF 10.0E-3 T/D := ENDOF \ 10 SEC/DIV
34 OF 20.0E-3 T/D := ENDOF \ 20 SEC/DIV
35 OF 50.0E-3 T/D := ENDOF \ 50 SEC/DIV
36 OF 100.0E-3 T/D := ENDOF \ 100 SEC/DIV
ENDCASE

; \\ COLON DEF TO COMPUTE THE DELAY TIME

: GET.DLT
FDES[20] 2 16 ** * \ SHIFT HIGH BYTE OVER
FDES[21] 2 8 ** * \ SHIFT NEXT BYTE OVER
FDES[22] ++ \ GET LAST BYTE ADD
FDES[19] 255 >= \ IS SIGN BYTE NEG ?
IF
2 24 ** - DLYTM := \ IF SO, MAKE NEG
ELSE
DLYTM := \ ELSE, LEAVE AS IS
THEN
-1 6 SCI.FORMAT
DLYTM 50 / T/D * DLYTM := \ COMPUTE IN SECONDS
;
\\ COLON DEFINITION TO GET SAMPLING INTERVAL

: GET.INTERVAL
-1 4 SCI.FORMAT
FDES[11]
CASE
11 OF 0.200E-9 SMPINT := ENDOF \ .2 NSEC/POINT
12 OF 0.400E-9 SMPINT := ENDOF \ .4 "
13 OF 0.800E-9 SMPINT := ENDOF \ .8 "
16 OF 10.0E-9 SMPINT := ENDOF \ 10 "
17 OF 20.0E-9 SMPINT := ENDOF \ 20 "
18 OF 40.0E-9 SMPINT := ENDOF \ 40 "
19 OF 80.0E-9 SMPINT := ENDOF \ 80 "
20 OF 200E-9 SMPINT := ENDOF \ 200 "
21 OF 400E-9 SMPINT := ENDOF \ 400 "
22 OF 800E-9 SMPINT := ENDOF \ 800 "
23 OF 2.00E-6 SMPINT := ENDOF \ 2 USEC/POINT
24 OF 4.00E-6 SMPINT := ENDOF \ 4 "
25 OF 8.00E-6 SMPINT := ENDOF \ 8 "
26 OF 20.0E-6 SMPINT := ENDOF \ 20 "
27 OF 40.0E-6 SMPINT := ENDOF \ 40 "
28 OF 80.0E-6 SMPINT := ENDOF \ 80 "
29 OF 200E-6 SMPINT := ENDOF \ 200 "
30 OF 400E-6 SMPINT := ENDOF \ 400 "
31 OF 800E-6 SMPINT := ENDOF \ 800 "
32 OF 2.00E-6 SMPINT := ENDOF \ 2 MSEC/POINT
33 OF 4.00E-6 SMPINT := ENDOF \ 4 "
34 OF 8.00E-6 SMPINT := ENDOF \ 8 "
35 OF 20.0E-6 SMPINT := ENDOF \ 20 "
36 OF 40.0E-6 SMPINT := ENDOF \ 40 "
40 OF 100E-9 SMPINT := ENDOF \ 100 NSEC/DIV
41 OF 1.00E-6 SMPINT := ENDOF \ 1 USEC/DIV
42 OF 10.0E-6 SMPINT := ENDOF \ 10 "
43 OF 100E-6 SMPINT := ENDOF \ 100 "
44 OF 1.00E-3 SMPINT := ENDOF \ 1 MSEC/DIV
45 OF 10.0E-6 SMPINT := ENDOF \ 10 "
ENDCASE

\ COLON DEFINITION TO GET NUMBER OF SWEEPS FOR AVG MODE

: GET.SWEEPS
FDES [ 73 ]
FDES [ 74 ]
SWAP 256 * + #SWPS :=

\ COLON DEFINITION TO TAKE IN A BLOCK OF DATA

: GET.SUBBLK
0 WAVE :=
ME LISTENER DS01 TALKER
BUFFER.LISTEN
UNLISTEN
WAVE UNPACK SUB[ 5 , 1000 ] \ UNPACK, SKIP HEADER AND
BYTE COUNT, TAKE 1000 PTS
200 MSEC.DELAY

\ COLON DEFINITION TO RECORD EACH DATA BLOCK

: GET.BLK
SEND.INTERFACE.CLEAR
WAVE [] GPIB.BUFFER
ME TALKER DS01 LISTENER
" CBLS," BLKsz 6 + ":" "CAT 32 " COMPRESS GPIB.WRITE
"RD," SOURCE "CAT", .DA, 1," CAT #PTS "." CAT SA "." CAT 32 "COMPRESS GPIB.WRITE
GET.SUBLK
BECOMES > BLK1
GET.SUBLK
BECOMES > BLK2
GET.SUBLK
BECOMES > BLK3
GET.SUBLK
BECOMES > BLK4
GET.SUBLK
BECOMES > BLK5
GET.SUBLK
BECOMES > BLK6
GET.SUBLK
BECOMES > BLK7
GET.SUBLK
BECOMES > BLK8
GET.SUBLK
BECOMES > BLK9
GET.SUBLK
BECOMES > BLK10
;
\ - COLON DEFINITION TO STORE WAVEFORMS ON DISK

: STORE.DATA.FILE
REGULAR.DATAFILE
FILE.TEMPLATE
4 COMMENTS
INTEGER DIM( 150 ) SUBFILE
INTEGER DIM( 1000 ) SUBFILE
11 TIMES
END
CR CR
." ENTER NAME OF FILE TO STORE DATA : "
"INPUT FILENAME ":=
CHDIR C:\ASYST\9400\DATA
FILENAME DEFER > FILE.CREATE
FILENAME DEFER > FILE.OPEN
"DATE 1 >COMMENT
"TIME 2 >COMMENT
CR CR ." ENTER A ONE LINE DESCRIPTION OF THE DATA"
CR ." NOT TO EXCEED 64 CHARACTERS"
"INPUT 3 >COMMENT
CR CR ." ENTER THE TIME OFFSET, REPPELLER DELAY"
CR ." PLUS PULSE GEN DELAY IN SECONDS: "
"INPUT TOFFSET ":=
TOFFSET 4 >COMMENT
1 SUBFILE FDES ARRAY > FILE
2 SUBFILE BLK1 ARRAY > FILE
3 SUBFILE BLK2 ARRAY > FILE
4 SUBFILE BLK3 ARRAY > FILE
5 SUBFILE BLK4 ARRAY > FILE
6 SUBFILE BLK5 ARRAY > FILE
7 SUBFILE BLK6 ARRAY > FILE
8 SUBFILE BLK7 ARRAY > FILE
9 SUBFILE BLK8 ARRAY > FILE
10 SUBFILE BLK9 ARRAY > FILE
11 SUBFILE BLK10 ARRAY > FILE
FILE.CLOSE
CHDIR C:\ASYST
;
\ COLON DEFINITION TO READ IN DATA FROM SCOPE AND
\ STORE DATA ON DISK

: GET.DATA
GET.DES \ GET DESCRIPTOR
GET.BLK \ READ BLOCKS OF
STORE.DATA.FILE \ DATA INTO TOKENS
STORE DATA ON DISK
;
\ COLON DEFINITION TO CONVERT Y VALUES

: YSCALE
128. - 32. / OFFSET 200. - 25. / -
200. VGAIN 80. + / *
FGAIN *
;
\ COLON DEFINITION TO READ WAVEFORM FROM DISK

: READ.DATA.FILE
CHDIR C:\ASYST\9400\DATA
" ENTER THE NAME OF THE DATA FILE: "
"INPUT FILENAME ":=
FILENAME DEFER> FILE.OPEN
CR ?COMMENTS
4 COMMENT> TOFFSET ":=
1 SUBFILE FILE>UNNAMED.ARRAY
BECOMES> FDES
VCALC
TIME.DIV
GET.DLT
GET INTERVAL
;
\ COLON DEFINITION TO SCALE AND PLOT X AND Y
\ AXIS FOR MASS SPECTRUM

: PLOT.AXIS
-1 4 SCI FORMAT
TOFFSET 32 "NUMBER
DLYTM -
1.0E6 *
1.0E4 SMPINT *
TOFFSET 32 "NUMBER +
DLYTM - 1.0E6 *
HORIZONTAL AXIS.FIT.ON WORLD.SET
ORIGIN YSCALE
RANGE YSCALE
VERTICAL AXIS.FIT.ON WORLD.SET
XY.AXIS.PLOT
;
\ COLON DEFINITION TO PLOT OUT THE MASS SPECTRUM

: GO.PLOT
PLOT.AXIS
1000 REAL RAMP 1. - SMPINT * TOFFSET 32 "NUMBER + DLYTM - 1.0E6 *
BECOMES> XTB
11 1 DO
XTB I 1 - 1000 * SMPINT * 1.0E6 * +
I 1 + SUBFILE FILE>UNNAMED.ARRAY YSCALE
XY.DATA.PLOT
LOOP
FILE.CLOSE
;
\ COLON DEFINITION TO TURN OFF GRID

: NO.GRID
HORIZONTAL AXIS.ON GRID.OFF
VERTICAL AXIS.ON GRID.OFF
;
\ ROUTINE TO SKIP FIRST SUB BLOCK IN PLOTTING IN ORDER TO ELIMINATE
\ LASER NOISE IN SCALING THE PLOT RANGE

: ELN.PLOT
PLOT.AXIS
1000 REAL RAMP 1. - SMPINT * TOFFSET 32 "NUMBER + DLYTM - 1.0E6 *
BECOMES> XTB
11 2 DO \ SKIP FIRST SUB BLOCK
XTB I 1 - 1000 * SMPINT * 1.0E6 * +
I 1 + SUBFILE FILE>UNNAMED.ARRAY YSCALE
XY.DATA.PLOT
LOOP
FILE.CLOSE
;
\ COLON DEFINITION TO REPLOT DATA WITHOUT HAVING TO READ IT IN
\ AGAIN. THIS DEFINITION WAS WRITTEN PRIMARILY SO THAT THE Y-AXIS
\ COULD BE ITERATIVELY SCALED. THIS IS ACCOMPLISHED BY CHANGING
\ THE VALUES OF THE SCALARS "ORIGN" AND "RANGE" AND REPLOTTING
\ THE DATA UNTIL A MORE SUITABLE SCALING IS ACHIEVED FOR THE MASS
\ SPECTRUM

: REPLOT
FILENAME DEFER> FILE.OPEN
NORMAL.DISPLAY
STACK.CLEAR
GO.PLOT
;
ASYST WAVEFORM ANALYSIS PROGRAM
FOR THE LECROY 9400A DIGITAL SCOPE
VERSION 1

JEFFREY W. FINCH 11/08/90 REVISED: 11/08/90

ASYST SYSTEM FILE IS ASYSTWA
FILENAME IS 9400ANS.ASC

BECAUSE ASYST 3.0 IS SUCH A MEMORY HOG AND SINCE THERE
IS NO WAY OF ASSIGNING THE NUMBER STACK TO EXPANDED
MEMORY, IT BECAME NECESSARY TO WRITE THIS PROGRAM
WHICH ONLY HAS THE FILE I/O, WAVEFORM ANALYSIS, AND
PLOTTER DRIVERS. THIS PROGRAM WAS WRITTEN SO THAT THE
SMOOTHING AND WAVEFORM ANALYSIS FUNCTIONS IN ASYST COULD
BE USED FOR HARD COPY PLOTS, ALL THE GPIB AND FILE INPUT
CODE HAS BEEN ELIMINATED AND THIS PROGRAM IS SOLELY FOR
WAVEFORMS WHICH HAVE ALREADY BEEN STORED ON DISK

REQUIRED OVERLAYS: FILE IO (DATAFILES.SOV), WAVEFORM
ANALYSIS (WAVEOPS.SOV), PLOTTER DRIVER (HPPLOTR.SOV)

20 STRING FILENAME
20 STRING TOFFSET

INTEGER SCALAR OFFSET
INTEGER SCALAR VGAIN
INTEGER SCALAR BPT
INTEGER SCALAR #SWPS
INTEGER SCALAR RANGE 256 RANGE :=
INTEGER SCALAR ORIGN 0 ORIGN :=
REAL SCALAR FGAIN
REAL SCALAR DLYTM
REAL SCALAR T/D
REAL SCALAR SMPINT
INTEGER DIM[ 100 ] ARRAY DESCR

*************** TOKENS ***************

TOKEN XTB EXP.MEM> XTB
TOKEN FDES EXP.MEM> FDES
TOKEN SSMSCALE EXP.MEM> SSMSCALE
TOKEN BLK1 EXP.MEM> BLK1
TOKEN BLK2 EXP.MEM> BLK2
TOKEN BLK3 EXP.MEM> BLK3
TOKEN BLK4 EXP.MEM> BLK4
TOKEN BLK5 EXP.MEM> BLK5
TOKEN BLK6 EXP.MEM> BLK6
TOKEN BLK7 EXP.MEM> BLK7
TOKEN BLK8 EXP.MEM> BLK8
TOKEN BLK9 EXP.MEM> BLK9
TOKEN BLK10 EXP.MEM> BLK10
TOKEN BLK11 EXP.MEM> BLK11
TOKEN BLK12 EXP.MEM> BLK12

\ COLON DEF TO CALCULATE THE THREE FACTORS FOR CONVERTING THE
\ INTEGER DATA POINTS INTO VOLTAGE VALUES

:VCALC
FDES [ 1 ]
CASE
22 OF 5.0E-3 FGAIN := ENDOF \ 5 mV
23 OF 10.0E-3 FGAIN := ENDOF \ 10 mV
24 OF 20.0E-3 FGAIN := ENDOF \ 20 mV
25 OF 0.050 FGAIN := ENDOF \ 50 mV
26 OF 0.100 FGAIN := ENDOF \ .1 V
27 OF 0.200 FGAIN := ENDOF \ .2 V
28 OF 0.500 FGAIN := ENDOF \ .5 V
29 OF 1.00 FGAIN := ENDOF \ 1 V
30 OF 2.00 FGAIN := ENDOF \ 2 V
31 OF 5.00 FGAIN := ENDOF \ 5 V
ENDCASE

FDES [ 2 ] VGAIN := \ GET THE VERTICAL GAIN

; \ COLON DEFINITION TO DETERMINE TIME/DIV

: TIME.DIV
-1 4 SCI.FORMAT
FDES [ 10 ] \ 10TH ELEMENT OF DESCRIPTOR
CASE
4 OF 2.00E-9 T/D := ENDOF \ 2 NSEC/DIV
5 OF 5.00E-9 T/D := ENDOF \ 5 NSEC/DIV
6 OF 10.0E-9 T/D := ENDOF \ 10 NSEC/DIV
7 OF 20.0E-9 T/D := ENDOF \ 20 NSEC/DIV
8 OF 50.0E-9 T/D := ENDOF \ 50 NSEC/DIV
9 OF 0.100E-6 T/D := ENDOF \ .1 USEC/DIV
10 OF 0.200E-6 T/D := ENDOF \ .2 USEC/DIV
11 OF 0.500E-6 T/D := ENDOF \ .5 USEC/DIV
12 OF 1.00E-6 T/D := ENDOF \ 1 USEC/DIV
13 OF 2.00E-6 T/D := ENDOF \ 2 USEC/DIV
14 OF 5.00E-6 T/D := ENDOF \ 5 USEC/DIV
15 OF 10.0E-6 T/D := ENDOF \ 10 USEC/DIV
16 OF 20.0E-6 T/D := ENDOF \ 20 USEC/DIV
17 OF 50.0E-6 T/D := ENDOF \ 50 USEC/DIV
18 OF 0.100E-3 T/D := ENDOF \ .1 MSEC/DIV
19 OF 0.200E-3 T/D := ENDOF \ .2 MSEC/DIV
20 OF 0.500E-3 T/D := ENDOF \ .5 MSEC/DIV
21 OF 1.00E-3 T/D := ENDOF \ 1 MSEC/DIV
22 OF 2.00E-3 T/D := ENDOF \ 2 MSEC/DIV
23 OF 5.00E-3 T/D := ENDOF \ 5 MSEC/DIV
24 OF 10.0E-3 T/D := ENDOF \ 10 MSEC/DIV
25 OF 20.0E-3 T/D := ENDOF \ 20 MSEC/DIV
26 OF 50.0E-3 T/D := ENDOF \ 50 MSEC/DIV
27 OF 0.100 T/D := ENDOF \ .1 SEC/DIV
28 OF 0.200 T/D := ENDOF \ .2 SEC/DIV
29 OF 0.500 T/D := ENDOF \ .5 SEC/DIV
30 OF 1.00 T/D := ENDOF \ 1 SEC/DIV
31 OF 2.00 T/D := ENDOF \ 2 SEC/DIV
32 OF 5.00 T/D := ENDOF \ 5 SEC/DIV
33 OF 10.0 T/D := ENDOF \ 10 SEC/DIV
34 OF 20.0 T/D := ENDOF \ 20 SEC/DIV
35 OF 50.0 T/D := ENDOF \ 50 SEC/DIV
36 OF 100.0 T/D := ENDOF \ 100 SEC/DIV
ENDCASE
;

\ COLON DEF TO COMPUTE THE DELAY TIME

: GET.DLT
FDES [ 20 ] 2 16 ** * \ SHIFT HIGH BYTE OVER
FDES [ 21 ] 2 8 ** * \ SHIFT NEXT BYTE OVER
FDES [ 22 ] + + \ GET LAST BYTE, ADD
FDES [ 19 ] 255 >= \ IS SIGN BYTE NEG ?
IF
  2 24 ** - DLYTM := \ IF SO, MAKE NEG
ELSE
  DLYTM := \ ELSE, LEAVE AS IS
THEN
-1 6 SCIFORMAT
DLYTM 50 / T/D * DLYTM :=
;
\ COLON DEFINITION TO GET SAMPLING INTERVAL

: GET.INTERVAL
-1 4 SCIFORMAT
FDES [ 11 ]
CASE
11 OF 0.200E-9 SMPINT := ENDOF \ .2 NSEC/POINT
12 OF 0.400E-9 SMPINT := ENDOF \ .4 "
13 OF 0.800E-9 SMPINT := ENDOF \ .8 "
16 OF 10.0E-9 SMPINT := ENDOF \ 10 "
17 OF 20.0E-9 SMPINT := ENDOF \ 20 "
18 OF 40.0E-9 SMPINT := ENDOF \ 40 "
19 OF 80.0E-9 SMPINT := ENDOF \ 80 "
20 OF 200E-9 SMPINT := ENDOF \ 200 "
21 OF 400E-9 SMPINT := ENDOF \ 400 "
22 OF 800E-9 SMPINT := ENDOF \ 800 "
23 OF 2.00E-6 SMPINT := ENDOF \ 2 USEC/POINT
24 OF 4.00E-6 SMPINT := ENDOF \ 4 "
25 OF 8.00E-6 SMPINT := ENDOF \ 8 "
26 OF 20.0E-6 SMPINT := ENDOF \ 20 "
27 OF 40.0E-6 SMPINT := ENDOF \ 40 "
28 OF 80.0E-6 SMPINT := ENDOF \ 80 "
29 OF 200E-6 SMPINT := ENDOF \ 200 "
30 OF 400E-6 SMPINT := ENDOF \ 400 "
31 OF 800E-6 SMPINT := ENDOF \ 800 "
32 OF 2.00E-6 SMPINT := ENDOF \ 2 MSEC/POINT
33 OF 4.00E-6 SMPINT := ENDOF \ 4 "
34 OF 8.00E-6 SMPINT := ENDOF \ 8 "
35 OF 20.0E-6 SMPINT := ENDOF \ 20 "
36 OF 40.0E-6 SMPINT := ENDOF \ 40 "
40 OF 100E-9 SMPINT := ENDOF \ 100 NSEC/DIV
41 OF 1.00E-6 SMPINT := ENDOF \ 1 USEC/DIV
42 OF 10.0E-6 SMPINT := ENDOF \ 10 "
43 OF 100E-6 SMPINT := ENDOF \ 100 "
44 OF 1.00E-3 SMPINT := ENDOF \ 1 MSEC/DIV
45 OF 10.0E-6 SMPINT := ENDOF \ 10 "
ENDCASE
;
\ COLON DEFINITION TO GET NUMBER OF SWEEPS FOR AVG MODE

: GET.SWEEPS
FDES [ 73 ]
FDES [ 74 ]
SWAP 256 * #SWPS :=
;
\ COLON DEFINITION TO CONVERT Y VALUES
YScale
128. - 32. / Offset 200. - 25. / -
200. VGain 80. + / *
FGain *
;
\ COLON DEFINITION TO READ WAVEFORM FROM DISK

READ DATA FILE
CHDIR C:\ASYST\9400\DATA
."
" Enter the name of the data file: "
" Input filename " :=
FILENAME DEFER> FILE OPEN
CR?COMMENTS
4 COMMENT> TOFFSET " :=
1 SUBFILE FILE> UNNAMED ARRAY
BECOMES> FDES
VCALC
TIME DIV
GET DLT
GET INTERVAL
;
\ COLON DEFINITION TO SCALE AND PLOT THE
X AND Y AXIS FOR THE MASS SPECTRUM

PLOT AXIS
-1 4 SCI FORMAT
TOFFSET 32 " NUMBER
DLYTM -
1.0E6 *
1.0E4 SMPINT *
TOFFSET 32 " NUMBER +
DLYTM - 1.0E6 *
HORIZONTAL AXIS FIT ON WORLD SET
ORIGIN YSCALE
RANGE YSCALE
VERTICAL AXIS FIT ON WORLD SET
XY AXIS PLOT
;
\ COLON DEFINITION TO PLOT MASS SPECTRUM

GO PLOT
PLOT AXIS
1000 REAL RAMP 1. - SMPINT * TOFFSET 32 " NUMBER + DLYTM - 1.0E6 *
BECOMES> XTB
I 1 DO
XTB I 1 - 1000 * SMPINT * 1.0E6 * +
I 1 + SUBFILE FILE> UNNAMED ARRAY YSCALE
XY DATA PLOT
LOOP
FILE CLOSE
;
\ COLON DEFINITION TO TURN OFF GRID

NO GRID
HORIZONTAL AXIS ON GRID OFF
VERTICAL AXIS ON GRID OFF
; ROUTINE TO SKIP FIRST SUB BLOCK IN PLOTTING IN ORDER TO ELIMINATE
\ LASER NOISE IN SCALING THE PLOT RANGE

: ELN.PLOT
PLOT.AXIS
1000 REAL RAMP 1. - SMPINT * TOFFSET 32 "NUMBER + DLYTM - 1.0E6 *
  BECOMES> XTB
11 2 DO \ SKIP FIRST SUB BLOCK
XTB I 1 - 1000 * SMPINT * 1.0E6 * +
I 1 + SUBFILE FILE>UNNAMED.ARRAY YSCALE
XY.DATA.PLOT
LOOP
FILE.CLOSE
;

\ SUBROUTINE TO SMOOTH THE DATA BEFORE PLOTTING

: SMOOTH.PLOT
PLOT.AXIS
.1 SET.CUTOFF.FREQ \ CUTOFF FREQUENCY FACTOR
  \ DEFAULT IS .1
1000 REAL RAMP 1. - SMPINT * TOFFSET 32 "NUMBER + DLYTM - 1.0E6 *
  BECOMES> XTB
11 2 DO \ SKIP FIRST SUBBLOCK TO
  \ TO ELIMINATE LASER NOISE
XTB I 1 - 1000 * SMPINT * 1.0E6 * +
I 1 + SUBFILE FILE>UNNAMED.ARRAY YSCALE BECOMES> SMSCALE
SMSCALE SMOOTH
BECOMES> SMSCALE
SMSCALE
XY.DATA.PLOT
LOOP
FILE.CLOSE
;

: REPlot
FILENAME DEFER> FILE.OPEN
NORMAL.DISPLAY
STACK.CLEAR
GO.PLOT
;
ASYST COLON DEFINITIONS TO CONVERT SUBFILES OF WAVEFORMS FROM THE LECROY 9400 SCOPE TO INDIVIDUAL FILES FOR USAGE WITH SPECTRACALC AND FOR COMBINING TWO ADJACENT SUBFILE ARRAYS INTO A SINGLE ARRAY AND STORING THE NEW ARRAY INTO A DATA FILE TO USE WITH SPECTRACALC. FILES WILL BE STORED ON A FLOPPY DISK IN DRIVE A. FILES STORED ON THE FLOPPY DISK CAN THEN BE IMPORTED INTO A VERSION OF SPECTRACALC WHICH HAS BEEN SET UP TO IMPORT ASYST DATA FILES.

9400DRV.ASC MUST BE LOADED UP BEFORE THIS PROGRAM IS LOADED INTO ASYST

JEFFREY W. FINCH
12/17/90 REVISED: 12/18/90

SYSTEM FILE IS ASYSTALT FILENAME IS CNVSC.ASC

20 STRING SUBFNAME

INTEGER SCALAR SFI
INTEGER SCALAR EFI
INTEGER SCALAR ILB

TOKEN TEMP EXP.MEM> TEMP
TOKEN PRT1 EXP.MEM> PRT1
TOKEN PRT2 EXP.MEM> PRT2
TOKEN COMBO EXP.MEM> COMBO

COLON DEFINITION TO CONVERT INDIVIDUAL SUBFILES TO DATA FILES FOR USE WITH SPECTRACALC

: CNVSC
" REMOVE THE ASYST DRIVER DISKETTE FROM DRIVE"
CR " A AND INSERT A DISK TO STORE SUBFILES"
CR READ.DATA.FILE FILE.CLOSE
CR CR " ENTER NUMBER OF THE STARTING SUBFILE: ":
#INPUT SFI :=
CR " ENTER NUMBER OF SUBFILES FOR CONVERSION: ":
#INPUT EFI :=
SFI EFI + SFI DO
CHDIR C:\ASYST\9400\DATA
FILENAME DEFER> FILE.OPEN I SUBFILE FILE>UNNAMED.ARRAY YSCALE BECOMES> TEMP FILE.CLOSE
REGULAR.DAYATFILE FILE.TEMPLATE
REAL DIM[ 1000 ] SUBFILE END
CR " ENTER A NAME FOR THE" I ." SUBFILE: " "INPUT SUBFNAME ":="
CHDIR A:\ SUBFNAME DEFER> FILE.CREATE SUBFNAME DEFER> FILE.OPEN 1 SUBFILE TEMP ARRAY>FILE FILE.CLOSE LOOP
CHDIR C:\ASYST

\ COLON DEFINITION TO TAKE TWO SUBFILE ARRAYS AND
\ COMBINE THEM, STORING THEM INTO A NEW DATA FILE
\ ON DRIVE A

; CATSC
CR ." REMOVE THE ASYST DRIVER DISKETTE FROM DRIVE A"
CR ." AND INSERT A DISK TO STORE COMBINED SUBFILE."
CR READ.DATA.FILE
FILE.CLOSE
CR ." ENTER THE NUMBER OF THE FIRST SUBFILE:  
#INPUT 1LB :=
CHDIR C:\ASYST\9400\DATA
FILENAME DEFER> FILE.OPEN
1LB SUBFILE FILE>UNNAMED.ARRAY YSCALE BECOMES> PRT1
1LB 1 + SUBFILE FILE>UNNAMED.ARRAY YSCALE BECOMES> PRT2
FILE.CLOSE
PRT1 PRT2 CATENATE BECOMES> COMBO
REGULAR.DATAFILE
FILE.TEMPLATE
REAL DIM[ 2000 ] SUBFILE
END
CR ." ENTER A FILENAME FOR THE NEW ARRAY:  
"INPUT SUBFNAME ":=
CHDIR A:\
SUBFNAME DEFER> FILE.CREATE
SUBFNAME DEFER> FILE.OPEN
1 SUBFILE COMBO ARRAY>FILE
FILE.CLOSE
CHDIR C:\ASYST
;
LIST OF REFERENCES


77. Ibid, pp 18-20.
78. Ibid, p 30.
85. Ibid, p 43.
86. Ibid, p 51 and p 53.

90. Wiza, J.L., Nuclear Instruments and Methods, (1979), 162, 201.


