producible to about ±10%, and a constant base pressure was reached prior to detection.

Average mass measurement errors for EI and CI measurements were approximately the same although the errors in the EI mode were higher than expected (based on previous GC/FTMS results (*4*)). These higher errors likely resulted from the compromise between the conflicting requirements for accurate mass measurement and chemical ionization. Optimum mass measurement accuracies are obtained for EI spectra as space-charge effects are minimized; best results are obtained when the emission current is low (<120 nA), the electron beam time is short, and low trap potentials (0.3–0.5 V) are used. For chemical ionization, however, a higher trap potential (1.0 V) is required to minimize the loss of signal observed due to inefficient trapping during the long delays necessary to achieve base pressures. In addition, to obtain an abundant yield of CH_5^+ and $C_2H_5^+$ in the presence of the GC effluent, it is necessary to use high emission currents (>500 nA). Compromise conditions included a trap potential of 0.5 V and an emission current in excess of 300 nA.

Under the conditions used for this alternate EI–CI GC/FTMS analysis, it was possible to obtain approximately 2–3 CI and 2–3 EI spectral files per chromatographic peak. Excellent S/N was obtained for CI spectra even though only one scan per file was collected (see Figure 2), presumably because column effluent continuously entered the analyzer cell during the 700-ms delay, allowing CI to take place. Ideally, this delay should be minimized to permit either ensemble averaging for increased spectral S/N or better chromatographic time resolution. However, because of the low conductance in the current system, this was not possible. Improved conductance or the use of a differentially pumped dual cell design would be expected to improve performance (*8*). Ejection of excess reagent ions, which would improve resolution and mass measurement accuracy at shorter pump down times, was unnecessary with the the 700-ms delay used in this analysis.

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Tandem Quadrupole–Fourier Transform Mass Spectrometry of Oligopeptides

Sir: Fourier transform mass spectrometers provide a potentially attractive alternative to magnetic sector, quadrupole, and time-of-flight instruments for the characterization of large biological molecules (*1–3*). Equipped with superconducting magnets, Fourier transform instruments are expected to operate with a mass range in excess of 10 000 and a resolution of at least 10 000 at this mass. Fourier transform instruments function as ion storage devices and can therefore accumulate ions produced in low abundance from small amounts of sample. In addition, all masses in a spectrum can be recorded simultaneously at low resolution without sample ion destruction (*4*). Because of these two features, it should be possible to record complete mass spectra at the picomole sample level for molecules having molecular weights of several thousand. Direct analysis of biological molecules in mixtures should also be possible by using the double resonance technique to eject unwanted species prior to mass analysis of the ions stored in the cell. Consecutive collision-activated dissociation (*5, 6*) or laser photodissociation experiments (*7–10*) are expected to provide detailed structural information on the population of stored $(M + H)^+$ ions. Release of kinetic energy during ion fragmentation under the above experimental conditions severely restricts the resolution that can be achieved in spectra recorded on sector instruments. Mass measurement on Fourier transform mass spectrometers is independent of ion translational energy. Consequently, main beam and daughter ion spectra can both be recorded at high resolution.

One necessary requirement for the realization of the long ion storage times, picomole detection limits, and ultrahigh-resolution mass analysis on large biomolecules is that the ion cyclotron resonance cell in the Fourier transform instrument must be maintained at or below 10^{-8} torr. Unfortunately glycerol and other liquid matrices employed in the highly successful particle bombardment ionization methods all have vapor pressures in excess of 10^{-6} torr. Interfacing these techniques with a Fourier transform mass spectrometer has proved to be difficult.

Recently, two approaches have been suggested for overcoming problems associated with high pressure accompanying sample introduction and ionization in Fourier transform instruments. The first involves use of a differentially pumped, two-compartment cell within a conventional Fourier transform mass spectrometer. Nicolet Instruments now markets an instrument embodying this concept. The second approach utilizes a tandem quadrupole–Fourier transform mass spectrometer. In this instrument, sample introduction and ionization are carried out in a differentially pumped quadrupole ion source and only the ions of interest are then transferred to the ion cyclotron resonance cell for mass analysis (*11, 12*). Results presented in an earlier paper demonstrated the feasability of using this type of instrument for mass analysis of ions produced by cesium bombardment of nonvolatile samples dissolved in a volatile liquid matrix (*13*). At that time the instrument was operating with a prototype pumping system of marginal capacity. Pressure in the ion cyclotron cell could only be maintained at 2×10^{-7} torr, with or without sample in the ion source. As a result, much of the data obtained was of limited analytical utility.

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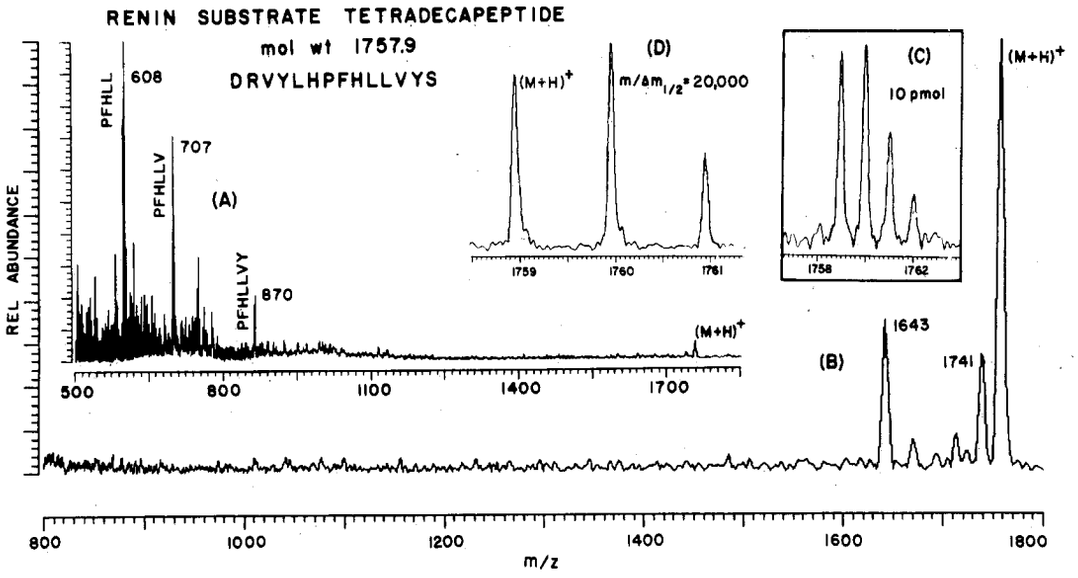

Figure 1. Mass spectra of renin substrate tetradecapeptide, DRVYLHPFHLLVYS, mol wt 1757.9: (A) broad-band mode on 100 pmol of sample with Q1 and $\omega 2$ set to reject ions below m/z 500 and between m/z 50 and 500, respectively; (B) broad-band mode on 100 pmol of sample with Q1 and $\omega 2$ set to reject ions below m/z 1600 and between m/z 50 and 800, respectively; (C) 10-pmol sample; (D) narrow-band mode on 100-pmol sample.

Here we present data on an improved version of the tandem quadrupole–Fourier transform mass spectrometer. The instrument is now operating with three cryogenic pumps that maintain the pressure of the system below 10^{-8} torr plus a pulsed cesium ion gun to minimize sample consumption during the ionization step.

EXPERIMENTAL SECTION

Tandem Quadrupole–Fourier Transform Mass Spectrometer. A schematic and description of this instrument appeared in an earlier publication (*13*). Described here are the modifications made to the instrument for the present work. For increased pumping speed, the three oil diffusion pumps on the system have been replaced with three Model HV-202-6C cryogenic pumps cooled by two Model 204SL compressors from Air Products, Allentown, PA. Pneumatically operated high-vacuum gate valves, Model 10044-UE40 from VAT Inc., Woburn, MA, separate each cryogenic pump from the vacuum manifold. Estimated pumping speed for each of the cryogenic pumps is 680 L s^{-1} of air. Measurements made with an ion gauge placed on the vacuum manifold at a point just beyond the entrance to the guiding quadrupole indicate that the tandem quadrupole–Fourier transform mass spectrometer now operates at a pressure of $(0.5–3.0) \times 10^{-9}$ torr.

Sample ionization is accomplished by using glycerol or thioglycerol as the liquid matrix and a cesium ion gun from Antek, Inc., Palo Alto, CA (*14*). In the normal operation of this gun the cesium ion source serves as an anode and floats at a variable potential, typically 6–10 keV. The anode is separated from the liquid matrix by extractor and focusing lenses which float at 95% and 90% of the anode potential, respectively. To minimize sample consumption, the above system has now been modified to operate in a pulsed mode under control of the IonSpec data system. Cesium ions are generated continuously but are pulsed onto the sample probe by switching the potential of the extractor lens from a value 105% to 90% that of the anode. The width of the pulse can be set as low as 1 ms while the pulse frequency operates as high as 200 Hz.

In addition to the above changes, the electronics for the two quadrupoles have been modified to operate at a frequency of 1.18 MHz. In the rf only mode the system now functions with a high mass cutoff above mass 10 000 and a low mass cutoff that can be set anywhere below mass 2000. The low mass cutoff allows the quadrupoles to reject most ions below a preset mass value and is employed here to exclude abundant low mass fragment ions produced from both the liquid matrix and the sample under particle bombardment ionization conditions. If allowed to enter the ion cyclotron resonance cell, these ions would quickly exceed the capacity of the cell and impair the ability of the instrument to detect weak signals at the high mass end of the spectrum.

Biological Samples. Bradykinin, gramicidin S, renin substrate tetradecapeptide, melittin, and vitamin B_{12} were purchased from Sigma Chemical Co., St. Louis, MO, and were used without further purification.

Operation of the Tandem-Quadrupole Fourier Transform Mass Spectrometer in Conjunction with a Particle Bombardment Ion Source. Unless otherwise specified, all samples used in the present study were prepared by adding 1 μL of a 100 pmol μL^{-1} solution of peptide in 5% acetic acid to 1 μL of glycerol, thioglycerol, or 1/1 thioglycerol–glycerol on a stainless steel probe. A positive potential of 1–6 V was placed on the probe after it had been inserted into the Finnigan Model 4500 ion source. The offset potentials on quadrupoles 1 and 2 were typically −30 V. Typical low mass cutoff values on quadrupoles 1 and 2 were in the range 200 to 2000 daltons. Potential applied to the trapping plates on the cell was typically +2 to +6 V. Receiver and transmitter plates were maintained at a dc potential of 0 V.

After the above parameters were set, mass spectra were acquired by using a series of pulses controlled by the data system. The first, or quench pulse, applied potentials of +10 and −10 V to the last trapping plate and was employed to clear the cell of all charged particles. The second, or ionization pulse, lowered the voltage on the extractor lens of the cesium ion gun and allowed cesium ions to impact on the sample matrix. Ionization pulses employed in the present study had a duration of 200–1000 ms. After a short delay, typically 100 ms, an ejection pulse, $\omega 2$, containing a range of rf frequencies ejects unwanted ions at the low mass end of the spectrum. Following an additional delay of 50–5000 ms, a detect pulse, $\omega 1$, containing a second range of rf frequencies corresponding to m/z values between 200 and 10,000 was applied to the transmitter plates. This second pulse of rf, having an amplitude of 8 V peak to peak and a duration of 2 ms, accelerates the ions trapped in the cell and causes them to move coherently at their characteristic cyclotron frequencies. Ion image currents induced by the ions on the cell receiver plates were detected, amplified, and digitized. The resulting time-averaged signal was then converted to the desired mass spectrum by using a 16K Fourier transform.

RESULTS AND DISCUSSION

Renin Tetradecapeptide Substrate. Figure 1 shows mass spectra of renin substrate tetradecapeptide obtained by bombarding sample at the 10–100 pmol level in 1/1 thioglycerol–glycerol with 8-keV cesium ions for a period of 1 s. Sample ions so produced were then transmitted through the fringing fields of a 7-T magnet with the aid of two rf only

quadrupoles and stored in an elongated ion cyclotron resonance cell. No effort was made to decelerate the ions before or after they entered the cell. To avoid overpopulation of the cell with low mass fragments produced from both sample and liquid matrix during the ionization process and/or via metastable decomposition pathways, the rf voltage on quadrupole 1 (Q1) was set to reject ions below m/z 500. A rf pulse, $\omega 2$, containing frequencies corresponding to m/z 50 to 500 was also employed to excite and eject low mass fragments from the cell prior to mass analysis of the stored ion population. After a delay of 400 ms, ions in the mass range of 500 to 5000 daltons were excited with another rf pulse, $\omega 1$. The resulting image currents were then detected, amplified, digitized, and Fourier transformed. Data from five such experiments were summed to generate the spectrum in Figure 1A.

Note that Figure 1A contains an abundant $(M + H)^+$ ion at m/z 1758.9 as well as a large number of fragment ions in the mass range from 500 to 1200 daltons. Fragment ions observed in highest abundance are of type $B_xY_z'^+$ and have formulas corresponding to $H(NHCHRCO)_n^+$. Formation of these ions probably occurs by selective protonation of the highly basic secondary nitrogen in the amide linkage involving proline at residue 7 in the peptide. Cleavage of this amide bond with migration of a hydrogen to the proline nitrogen would generate a $Y_8''^+$ ion (*15*) having the formula, $H_2(^+NHCHRCO)_8OH$ and containing the last eight amino acids in the chain. Migration of the proton to amide linkages following amino acids 11, 12, and 13 and subsequent cleavage at these points would produce the observed fragment ions. Cleavage of the above type is always one of the dominant pathways observed in the low-energy collision-activated dissociation of $(M + H)^+$ ions derived from proline-containing peptides.

The effect of $\omega 2$ and the Q1 rf setting on the spectrum is illustrated in Figure 1B. To obtain this spectrum the rf on Q1 was set to reject ions below m/z 1600 and $\omega 2$ was employed to excite and eject residual ions between m/z 50 and 800 transmitted by the quadrupoles or formed by metastable decomposition. The detect pulse excited ions in the mass range 800–8000 daltons, otherwise all other conditions were identical with those used to obtain the spectrum in Figure 1A. In Figure 1, parts A and B, the base peak in the spectrum is displayed with a relative abundance of 100. Since low mass ions are either rejected by Q1 or ejected by $\omega 2$ prior to mass analysis, Figure 1B now contains only ions above m/z 1600. The total ion current in the $(M + H)^+$ ion at m/z 1758.9 is essentially the same in both spectra. By use of the above experimental protocol in conjunction with the pulsed cesium ion gun, it should be possible to generate, store, and accumulate ion characteristic of the molecular weight of peptides at the subpicomole level without overpopulating the cell with low mass fragments and thus reaching the point where space charge phenomena adversely affect the performance of the instrument. Software limitations on our present data system prevent us from attempting this experiment. Without the capability to accumulate ions generated from a series of short ionization events, detection limits for the renin substrate tetradecapeptide are at the 3–5 pmol level. Figure 1C shows the molecular weight region of a spectrum taken on a 10-pmol sample. Resolution achieved in the narrow band mode using a 16K transform on the 80-ms transient obtained from a 100-pmol sample of renin substrate tetradecapeptide is shown in Figure 1D.

Successful molecular weight determinations on large biomolecules by Fourier transform mass spectrometry requires that the $(M + H)^+$ ion have a lifetime between 100 and 10 000 ms. This is to be contrasted with the situation in time-of-flight and magnetic sector instruments where mass analysis is complete in 10–500 μs. Experiments conducted under plasma desorption conditions on a time-of-flight instrument indicate that as little as 0.01% of the total sample ion current arrives at the detector as intact $(M + H)^+$ ions (*16*). In the case of chlorophyll *a*, mol wt 892, 99% of the ions characteristic of sample molecular weight undergo metastable decomposition 10–90 ns after the ionization event. Of those that remain, only 1.1% survive the 67 μs journey to the detector (*16*). If this trend were to continue into the millisecond time frame, few if any $(M + H)^+$ ions would be observed on a Fourier transform mass spectrometer.

To gain insight into the distribution of ion lifetimes observed for ions desorbed from a liquid matrix by cesium ion bombardment, several experiments were performed on a sample of renin substrate tetradecapeptide at the 100-pmol level. Features of the tandem-quadrupole Fourier transform instrument pertinent to these experiments are as follows. Ions enter the rf-only quadrupoles a few microseconds after ionization. Fragmentation occurring during this period is therefore indistinguishable from that accompanying the ionization event. Total transit time through the Q1 and Q2 is on the order of a few milliseconds for $(M + H)^+$ ions having m/z values near 2000. The $(M + H)^+$ ions that decompose to fragments having m/z values below the cutoff set by the rf voltage on Q1 and Q2 are rejected and lost. Those that decompose to fragment ions having masses above the set mass cutoff reach the cell intact and appear at the m/z value of the daughter ion. Those that fall apart in the cell during the 500-ms interval between ionization and detection also appear as fragment ions in the mass spectrum.

In the first experiment, the duration of the ionization pulse was set for 1 s, the rf voltage on Q1 and Q2 was set to reject ions below m/z 100, $\omega 2$, the ejection pulse, was omitted, and the detect pulse, $\omega 1$, was initiated 500 ms after the end of the ionization period. Under the above experimental conditions, the ion current observed between m/z 100 and 500 exceeded that obtained above m/z 500 in Figure 1A by more than 2 orders of magnitude.

Experiment two was conducted with an ionization pulse of 1 s, rf voltage on Q1 and Q2 set to exclude ions below m/z 1600, an $\omega 1$ pulse to eject ions having m/z values between 50 and 800, and a detect pulse that was initiated after a delay period of 0.5, 1, 3, 5, and 90 s. Results obtained after a delay period of 500 ms are shown in Figure 1B. No change in the spectrum was observed after a delay of 5 s. With a delay period of 90 s the observed ion current for the $(M + H)^+$ ion decreased by 50%. Fragment ion abundance failed to increase significantly, so diffusion to the walls of the cell rather than metastable decomposition is probably responsible for the observed ion losses.

The above results support the thesis that a large fraction of the desorbed $(M + H)^+$ ions undergo metastable deomposition in the first few microseconds. Fortunately the experiments also show that a small but analytically significant population of $(M + H)^+$ ions survive for several milliseconds. A large percentage of these latter ions remain stable toward fragmentation for an additional period amounting to several tens of seconds and probably minutes. Additional experiments to document the range of lifetimes exhibited by $(M + H)^+$ ions from several other large biological molecules will be conducted following modification of the software that is presently employed to control the operation of the instrument.

Ions most likely to survive for periods of seconds following desorption under particle bombardment conditions are those that leave the surface from points several angstroms removed from the site of projectile impact and then undergo collisional stabilization as they pass through the dense layer of gaseous neutrals just above the surface of the liquid matrix (*17*).

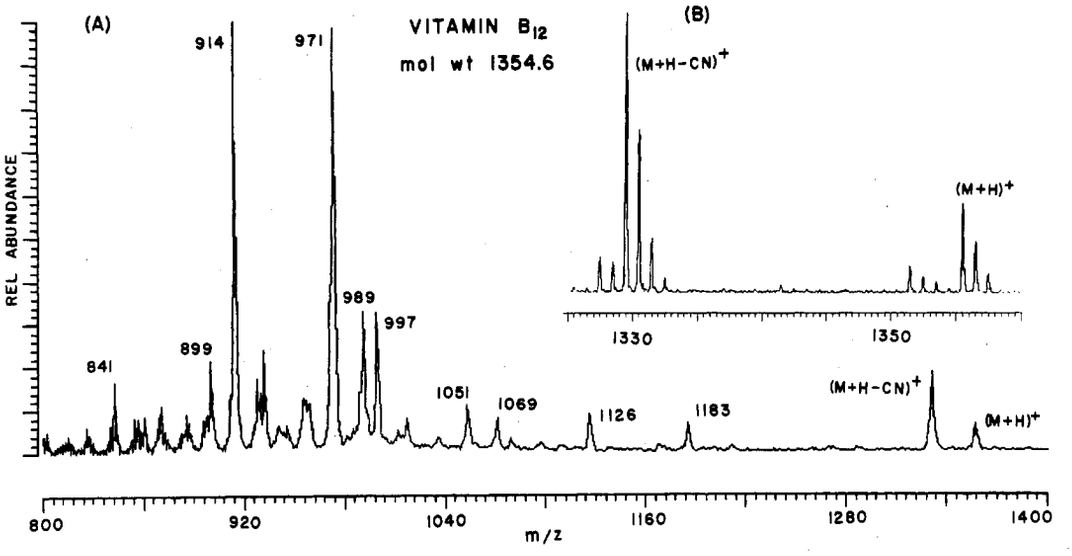

Figure 2. (A) Broad-band mass spectrum of vitamin B_{12} obtained at the nmol sample level with Q1 set to reject ions below m/z 800. (B) Narrow band mode with Q1 and $\omega 2$ set to eject ions below m/z 1000 and between 50 and 1000, respectively.

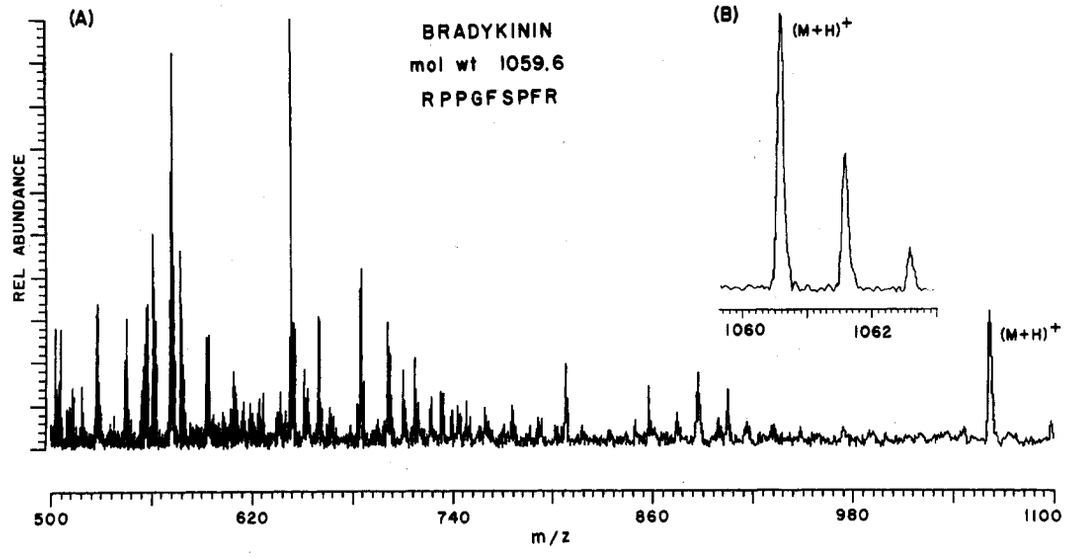

Figure 3. Mass spectrum of bradykinin, RPPGFSPFR, mol wt 1159.6: (A) broad-band mode on 1 nmol of sample with Q1 and $\omega 2$ set to eject ions below m/z 500 and between m/z 50 and 500, respectively; (B) narrow-band mode with Q1 and $\omega 2$ set to eject ions below m/z 1000 and between m/z 50 and 1000, respectively.

Alternately the desorbed $(M + H)^+$ ions could leave the surface with a cluster of attached solvent molecules and then suffer metastable decomposition reactions in which the solvent molecules are stripped away and remove part of the excess internal energy of the desorbed ion. Further reduction in the internal energy of large organic ions can result if emission of infrared radiation from the ion competes favorably with metastable decomposition (*18*).

Vitamin B_{12}. Mass spectra of vitamin B_{12} have been recorded with a number of different ionization techniques and instruments (*19*, *20*). Of particular interest here are the results obtained by using fast atom bombardment on a magnetic sector instrument (*19*) and cesium ion bombardment of a solid sample matrix on a conventional Fourier transform instrument equipped with a 3-T magnet (*20*). Initial spectra obtained using the latter technique contained abundant ions corresponding to a cesium cationized dimer, $[(B_{12})_2 + Cs - 2CN]^+$, and monomer, $(B_{12} + Cs - CN)^+$, at m/z 2792 and 1462, respectively. Fragment ions derived from the monomer and dimer were also present in somewhat lower abundance. Of additional interest was the finding that the relative abundance of ions derived from the dimer increased with the time the sample was exposed to the cesium ion beam.

In contrast to the above situation, spectra of vitamin B_{12} obtained under conventional fast atom bombardment conditions show a large number of fragment ions above m/z 800, the most abundant of which occur at m/z 1329 and 971 (*19*). An $(M + H)^+$ ion is also observed but carries less than 0.5% of the sample ion current above m/z 800. Figure 2A displays the mass spectrum of vitamin B_{12} produced on our tandem-quadrupole Fourier transform mass spectrometer. Data were obtained in the broad-band mode with the rf voltage on Q1 set to exclude ions having m/z values below 800, with $\omega 2$ turned off, and with an excitation pulse that excited ions over the mass range 800–5000 daltons. The spectrum in Figure 2A is qualitatively similar to that obtained by fast atom bombardment on a sector instrument. Structural assignments for the labeled ions in Figure 2A can be found in an earlier publication (*19*). A spectrum, obtained in the narrow band mode, of ions in the molecular weight region of vitamin B_{12} is shown in Figure 2B.

Bradykinin and Gramicidin S. Shown in Figures 3 and 4 are the mass spectra of bradykinin, mol wt 1059.6, and gramicidin S, mol wt 1140.7. Both sets of data were obtained with the rf on Q1 set to reject ions below m/z 500 and with $\omega 2$ set to eject ions between m/z 50 and 500. Bradykinin has

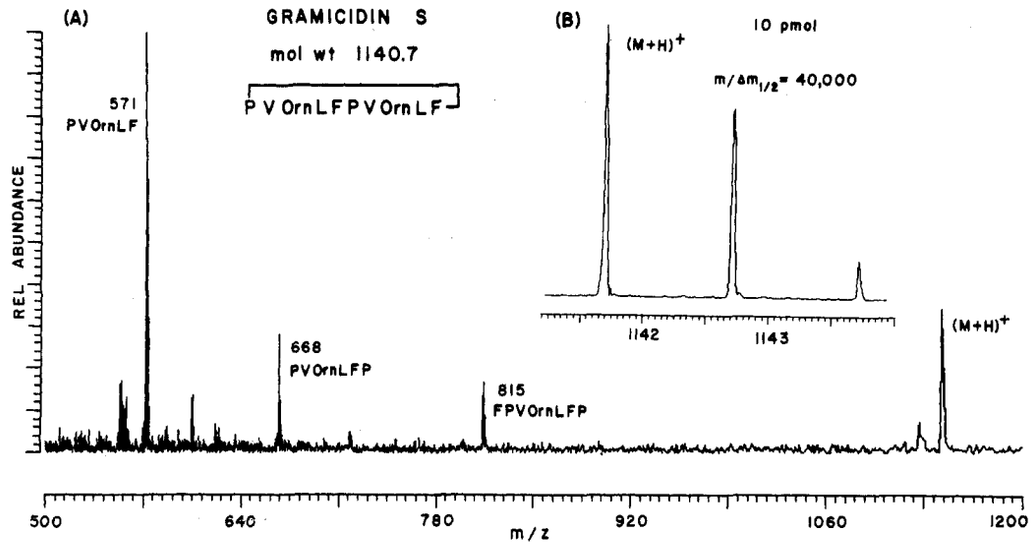

Figure 4. Mass spectrum obtained from one scan on 10 pmol of gramicidin S: (A) broad-band mode with Q1 and $\omega 2$ set to eject ions below m/z 500 and between m/z 50 and 500, respectively; (B) narrow-band mode with Q1 and $\omega 2$ set to eject ions below m/z 1000 and between m/z 50 and 1000, respectively.

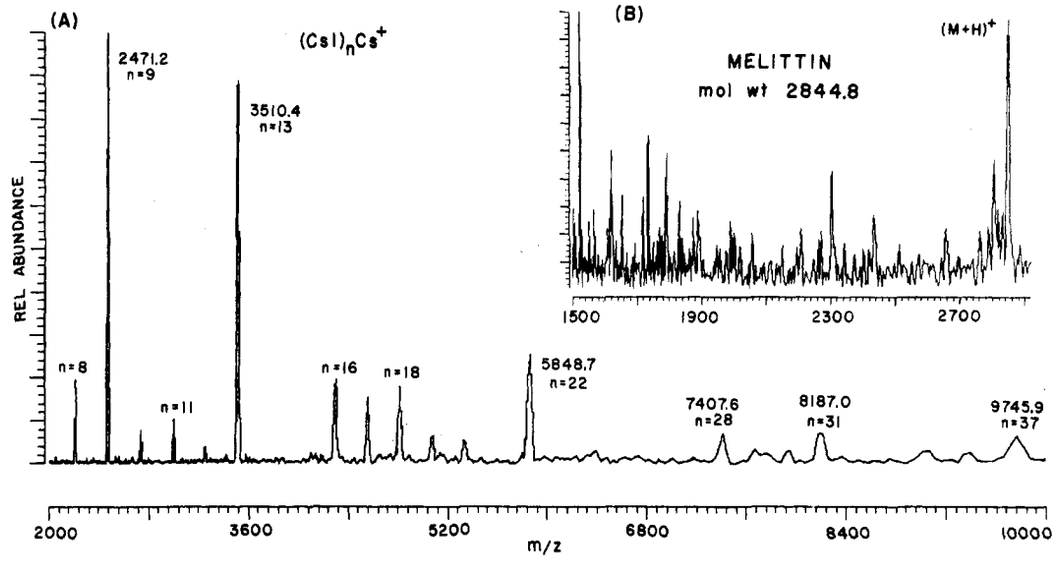

Figure 5. (A) Broad-band mass spectrum of cesium iodide obtained with Q1 and $\omega 2$ set to eject ions below m/z 2000 and between m/z 50 and 1000, respectively. (B) Broad-band mass spectrum of melittin, GIGAVLKVLTTGLPALISWIKRKRQQ-NH_2, mol wt 2844.8, obtained at the 100-pmol sample level with Q1 and $\omega 2$ set to eject ions below m/z 1500 and between m/z 50 and 1500, respectively.

been studied previously by fast atom bombardment on a sector instrument (*21*) as well as by laser desorption on a conventional Fourier transform mass spectrometer equipped with a 3-T magnet (*22*). In the fast atom bombardment spectrum, $(M + H)^+$ is the most abundant ion above m/z 300 and carries about 3% of the total sample ion current. Fragment ions sufficient to deduce the complete sequence of amino acids in the peptide are also observed. This result stands in contrast to the published laser desorption spectrum. The latter is dominated by fragment ions, the most abundant of which occur in the mass range between 950 and 1000 daltons. The $(M + H)^+$ ion is present but carries less than 1% of the total ion current. Spectra recorded on the tandem quadrupole–Fourier transform instrument resemble the fast atom bombardment spectra in that the $(M + H)^+$ ion carries 2–4% of the total ion current. Fragment ions sufficient to deduce the primary structure of the peptide are also observed. Detection limits for bradykinin are a factor of 10 higher than those realized for the renin substrate tetradecapeptide above.

Gramicidin S in a potassium bromide matrix has been studied by laser desorption on a Fourier transform instrument and affords a spectrum dominated by an $(M + K)^+$ ion at m/z 1179.7 (*22*). Spectra acquired under the conditions employed in the present work also contain a relatively small number of ions. The $(M + H)^+$ ion carries 25% of the total sample ion current. Ions of type $B_xY_z'^+$, discussed above, dominate the fragmentation pattern. Ionization of gramicidin S from a liquid matrix by particle bombardment appears to be an exceptionally facile process. Spectra displayed in Figure 4 were obtained with a single scan on 10 pmol of sample. Figure 4B shows the narrow band spectrum recorded on 10 pmol of gramicidin S. Resolution of 40 000 was obtained by performing a 16K transform on an 800-ms transient. Detection limits for this compound are more than 2 orders of magnitude lower than that for the renin substrate tetradecapeptide.

Melittin and Cesium Iodide. Figure 5A and Figure 5B show mass spectra obtained on a solid sample of cesium iodide and the 26 residue peptide melittin, mol wt 2844.9, respectively. Melittin has been studied previously under fast atom bombardment conditions and affords a spectrum containing a relatively weak signal for the $(M + H)^+$ ion, $S/N < 10$ (*23*, *24*). The molecular weight region of the spectrum obtained

on the tandem quadrupole–Fourier transform instrument for melittin at the 100 pmol level is displayed in Figure 5A. The S/N ratio achieved in this experiment is clearly substantially less than that observed for the other peptides discussed above. This spectrum is highly reproducible, however, and melittin at the 100-pmol level is often employed to test the tuning of the instrument. Glucagon and the insulin B chain, peptides having molecular weights in the range 3300–3500 daltons, afford signals for $(M + H)^+$ ions that are about the same as that observed for melittin. Insulins, in the molecular weight region 5600–5800 daltons, afford signals for $(M + H)^+$ ions that are barely visible above background on the present instrument. In the case of solid cesium iodide, Figure 5B, ions are readily observed out to m/z 9746, a limit imposed by our electronics and the software package on our present data system, but the S/N and resolution both deteriorate rapidly above m/z 3510.

To make the tandem quadrupole–Fourier transform mass spectrometer perform routinely in the mass range above m/z 3000 on biological samples at the subnanomole level will require improvements in both the electronics and data system. Efforts are presently under way to modify both the excitation and detection circuitry, to increase the computing power of the data system beyond 16K transforms, and to alter the software controlling the instrument to permit selective accumulation of high mass ions in the cell prior to mass analysis.

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Registry No. Renin substrate tetradecapeptide, 98064-97-2; vitamin B_{12}, 68-19-9; bradykinin, 58-82-2; gramicidin S, 113-73-5; cesium iodide, 7789-17-5; melittin, 37231-28-0.

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Long Range Effects of the Aluminum Avoidance Principle

Sir: The structure of poorly ordered aluminosilicates formed by precipitation from neutral or acid solution of hydroxyalumina and silica species, is of interest because these materials can be the weathering products of volcanic glasses and of podzolized soils from nonvolcanic parent material. They are also useful cracking catalysts.

Poorly ordered aluminosilicates are believed to consist of a core of tetrahedral silicon with partial substitution of aluminum in 4-fold coordination (*1–4*). Charge generated in the core by the replacement of Si^{4+} by Al^{3+} is balanced by octahedral Al^{3+}. Infrared evidence (*5, 6*) suggests that these materials can also contain quantities of material which contain individual silicon tetrahedra bonded through oxygen to three octahedrally coordinated aluminums and one proton. This material can differ physically in that discrete tubes may or may not be observed by electron microscopy. The two forms are termed imogolite and protoimogolite, respectively.

NMR is an ideal method for detecting imogolite or protoimogolite (*7*). Hence, in this paper we use ^{27}Al and ^{29}Si high-resolution solid-state nuclear magnetic resonance techniques to analyze the chemical structure of synthetic gels. Besides confirming the earlier proposals concerning structure, the results demonstrate that poorly ordered aluminosilicates have more order than previously supposed. It is also shown

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