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TRIPLE QUADRUPOLE MASS SPECTROMETRY FOR DIRECT MIXTURE ANALYSIS--ETC(U)

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TRIPLE QUADRUPOLE MASS SPECTROMETRY FOR
DIRECT MIXTURE ANALYSIS AND STRUCTURE ELUCIDATION

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energy collision-induced dissociation process in the strong focusing RF¹⁵ quadrupole field. Detection limits for methane and nitrobenzene of 10⁻¹⁵ mole are shown. Analysis of a mixture of six components, including two isomers and an isobaric compound is presented. Chemical noise is virtually eliminated by the selection of both parent and fragment ion. An application of the system for structure elucidation is also described.

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DIRECT MIXTURE ANALYSIS AND STRUCTURE ELUCIDATION

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BRIEF

Triple quadrupole mass spectrometry is shown to be a powerful new technique for the direct analysis of mixtures and the elucidation of molecular structures by R.A. Yost of the University of Florida and C.G. Enke of Michigan State University.

TRIPLE QUADRUPOLE MASS SPECTROMETRY FOR
DIRECT MIXTURE ANALYSIS AND STRUCTURE ELUCIDATION

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A new technique of mass spectrometry is rapidly emerging in which tandem mass analyzers are used for separation and identification in a single instrument. In this technique (MS/MS), several ionic species are generated from a sample, ions of a particular mass are selected for fragmentation, the selected ions are fragmented by one of several possible techniques, and the resulting fragment ions are mass-analyzed. We recently introduced the concept of a triple quadrupole mass spectrometer as a particularly simple and efficient approach to selected ion fragmentation (1). The instrument consists of, in series, a dual chemical ionization/electron impact (CI/EI) sample ionization source, a quadrupole mass filter, an RF-only quadrupole that can be pressurized with a collision gas, a second quadrupole mass filter, and an electron multiplier, as shown in Figure 1. The ion fragmentation process is performed by collision-induced dissociation (CID) in which the ion acquires internal energy by collision with a neutral molecule. The RF-only quadrupole collision chamber provides focusing of scattered ions and is highly efficient (2). In this system, the selected ion fragmentation process can provide enhanced selectivity and discrimination over normal mass spectrometry without significant loss of sensitivity.

THE ADDED DIMENSION OF INFORMATION

The added information contained in the fragmentation spectrum of each source ion species is of great value in several areas of mass spectrometry, especially the elucidation of organic structures and the

analysis of mixtures. In structure elucidation applications, fragment ions of any mass which appear in a compound's normal mass spectrum can be selected with the first mass analyzer. This parent ion is further fragmented, and the mass spectrum of the resulting daughter ions is determined by scanning the second mass analyzer. A complete fragmentation map may be obtained by recording the mass spectrum of each fragment ion of a compound. Figure 2 is an example of such a map, for cyclohexane. Note that the normal electron impact mass spectrum, displayed along the diagonal (fragment ion m/z = parent ion m/z), is the only information available without the added dimension of selected ion fragmentation.

For analysis of mixtures, the molecular ions for each component can be produced by soft ionization such as chemical ionization or field desorption and then separated by the first mass analyzer. Thus the molecular ion species can be selected for one component at a time, the selected ion fragmented, and its fragmentation mass spectrum obtained by scanning the second analyzer. The added dimension in this case is the selectivity and discrimination achieved through mass separation of the molecular ions of the several components. The elimination of chemical noise that results can often improve the detection limit of the mass spectral technique (3).

The use of mass spectral separation of the components of a mixture in MS/MS eliminates the time delays associated with the chromatographic separation used in GC/MS and LC/MS. Because all the components are available at any time and in any order, only those components of particular

interest need be analyzed. Each component may be selected for as much or as little time as is required to determine its identity and its quantity. Continuous analysis of a sample is possible in such applications as atmospheric analysis without the time delays associated with batch sampling for chromatographic analysis. Direct insertion probes and field or chemical desorption can be used to introduce involatile or thermally labile samples.

OTHER SELECTED ION FRAGMENTATION AND TANDEM MASS SPECTROMETERS

There are several other approaches to selected ion fragmentation, the most notable of which for analytical applications is Mass-Analyzed Ion Kinetic Energy Spectrometry, or MIKES (also called Collisional Activation Mass Spectrometry or CAMS, and Direct Analysis of Daughter Ions or DADI). This technique

makes use of a double-focusing mass spectrometer in which the magnetic sector precedes the electrostatic analyzer. Fragmentation between the sectors can be unimolecular (metastable ions) or collisionally induced. MIKES has been demonstrated as a technique for selected ion fragmentation in such applications as structure elucidation (4-8) and mixture analysis (3,9). The structure elucidation technique has been clearly described by Beynon (8). The technique for analysis of mixtures has been reviewed by Cooks in these pages (3). It is also possible to emulate the MIKES technique with a normal geometry double-focusing mass spectrometer (electric sector preceding the magnet) and a linked scan of both the electric sector field strength and either the magnetic field or accelerating voltage (10). Ions enter the CID collision chamber in sector instruments with 3-30 keV of kinetic energy. The mechanism of the CID process at these high energies is fundamentally different from the process at the low kinetic energies (3-50 eV) of ions in the triple quadrupole instrument (11).

True tandem mass spectrometers have been constructed to apply selected ion fragmentation techniques to the study of interactions between ions and molecules (12). Two quadrupoles in tandem have been employed to study ion-molecule reactions (13), and triple quadrupole systems have been applied to study the photodissociation of ions (14,15). However, it is the low-energy CID process in the center quad that makes the triple quadrupole spectrometer described here particularly well suited for analytical applications. Hunt and coworkers have recently reported on the analytical applications of a triple quadrupole instrument constructed in their laboratory (16).

MODES OF OPERATION

There are three fundamental control parameters in the triple quadrupole

mass spectrometer. These are the mass selected by the first mass analyzer, the presence or absence of collision gas in the quad collision chamber, and the mass selected by the second mass analyzer. These parameters may all be varied independently or in combinations to provide a variety of useful modes of operation as enumerated and described below:

1) In order to obtain a normal mass spectrum (only one stage of mass analysis), the first mass filter is scanned with the second and third quadrupoles in RF-only (total-ion) mode. The collision gas may be present or not, since it does not significantly affect the number of ions reaching the detector.

2) A scan of the third quadrupole while the first mass filter passes a specific mass produces a spectrum of all the daughter ions from the selected parent ion. If the collision gas is absent, the unimolecular decomposition products ("metastable" ion decomposition) will be measured.

3) The spectrum of all parent ions that fragment to produce a given daughter ion is observed by scanning the first mass filter with the third quadrupole fixed on the daughter ion mass.

4) The observation of a specific neutral mass loss is achieved by scanning both mass filters with a fixed difference in mass. The use of a double focusing mass spectrometer for neutral loss spectra has been suggested recently as a useful but complicated technique for structure elucidation (17).

5) A specific parent/daughter ion transition is selected in single reaction monitoring (18), a technique analogous to single ion monitoring in gas chromatography/mass spectrometry.

6) The quadrupole's linear mass scale and fast response permit rapid multiple reaction monitoring in which multiple parent/daughter ion pairs are observed.

MIXTURE ANALYSIS

As an example of the performance of the triple quadrupole mass spectrometer, the following sample which contains five components at equal concentration was chosen: 3-heptanone and n-heptanal (isomers of molecular weight 114), n-octane (isobaric with the other two at 114), cyclohexane (84), and 2-pentanone (86). The mixture was ionized by 70 eV EI, although CI would have simplified the mass spectrum. The CID spectra of the 114^+ ion from the individual components show unique fragmentation: 99^+ (M-15) for 3-heptanone, 96^+ (M-18) for n-heptanal, and 70^+ ($C_5H_{10}^+$) for n-octane. In the CID spectrum of the 114^+ ion in the mixture, it is possible to detect the individual components despite their being isomeric or isobaric. Figure 3 shows the CID spectrum of the 114^+ ion in the mixture as well as the reference CID spectra of 114^+ from the three pure compounds. The two isomers in the mixture may be identified with even greater confidence by obtaining the CID spectra of fragment ions produced by EI that are unique to the specific components. The CID spectra of 99^+ and 81^+ from the mixture exactly match the spectra of the 99^+ fragment from pure 3-heptanone and the 81^+ fragment from n-heptanal, respectively. The other two components are most readily identified in the mixture; the CID spectra of the molecular ions of pure cyclohexane (84^+) and 2-pentanone (86^+) are nearly perfect matches with the CID spectra of these ions from the mixture. The CID spectra obtained for 84^+ and 81^+ from the mixture are compared with reference spectra in Figure 3.

A sixth and unexpected component was discovered and identified in the mixture as well. The electron impact spectrum showed peaks at 120^+ and 105^+ which could not be attributed to any of the five known components. The CID spectra showed fragments from 120^+ at 105^+ , 43^+ , and 77^+ and fragments from 105^+ at 77^+ , 51^+ and 26^+ . Interpretation of these data suggested acetophenone

as the impurity, and a comparison with the reference CID spectra of 120^+ and 105^+ ions from pure acetophenone confirmed this. Careful study of the EI spectra of the individual components showed that the acetophenone was present as an impurity in the n-heptanal. A single standard addition experiment indicated an acetophenone concentration of approximately 5 parts per thousand in the n-heptanal and therefore 1 part per thousand in the mixture. These results demonstrate the ability of the triple quadrupole system to identify mixture components, including both isomers and isobaric compounds. The high sensitivity of the system for trace analysis is discussed in the instrument performance section.

STRUCTURE ELUCIDATION

As an example of a structure elucidation application, consider unknown 5.13 in McLafferty's classic text (19) on mass spectral interpretation. The EI spectrum shows molecular weight 120 with major peaks at 105 and 77. Considering the 77 peak (phenyl moiety) and 105 (loss of methyl), there are two possible compounds, $C_6H_5COCH_3$ and $C_6H_5CH(CH_3)_2$. Relying on the 121/120 ratio and the unusually small hydrogen-loss ions from 120 and 105, McLafferty concludes that the unknown is acetophenone, $C_6H_5COCH_3$. The structure of this unknown can be obtained in a direct manner using selected ion fragmentation on the triple quadrupole mass spectrometer. The large 43^+ peak in the EI spectrum corresponds to the remainder of the molecule [CH_3CO^+ or $(CH_3)_2CH^+$] after loss of 77 (C_6H_5). The CID spectrum of 43^+ is shown in Figure 4. Interpretation of the data indicates the fragmentations shown for CH_3CO^+ . The reference CID spectra of known ions shown in Figure 4 confirm that 43^+ from acetophenone matches the CID spectrum of CH_3CO^+ from acetone, but is significantly different from that of $(CH_3)_2CH^+$ from cyclohexane.

Thus, McLafferty's conclusion is confirmed. The process of structure elucidation of this unknown has been made simpler and more reliable by the added information available by selected ion fragmentation.

Ultimately, the formation and fragmentation of every ion in a compound's mass spectrum may be determined to yield a complete map of the fragmentation pathways for the molecule. Such a map, for cyclohexane, appears in Figure 2. This approach has been employed in a detailed study of the fragmentation of nonan-4-one (20). In that study, over 400 distinct collision-induced fragmentations have been observed, a ten-fold increase over the number previously observed in metastable studies (21). These include a number of new fragmentations of very low intensity such as loss of water from the α -cleavage ions. The high sensitivity of the triple quadrupole instrument has made it possible to observe these transitions.

DESCRIPTION OF INSTRUMENT

A scale drawing of the triple quadrupole spectrometer constructed at Michigan State University appears in Figure 5. The path length from source to detector is approximately 67 cm. The individual components of the system, including the source, quadrupoles, detector, vacuum system, and control electronics, are described below.

Samples may be introduced through a heated glass inlet system or a heated direct-insertion probe. The ion source is a Finnigan CI/EI model 3000. The first quadrupole mass filter is a standard Extranuclear Labs ELFS model with 0.95 cm diameter x 20 cm long rods and a mass range of 1-1000 amu. The center quadrupole is a homemade model with 0.954 cm diameter x 21.6 cm long stainless steel rods. Flat plate lenses on each end of the center quadrupole aid in

focusing the ion beam between quadrupoles. Another Extranuclear mass filter serves as the third quadrupole. It is identical to the first except that the small (0.2 cm diameter) entrance aperture has been removed. The axial ion energy in the three quadrupoles may be varied independently over the range -100 to +100 V, with -10 V being typical for positive ions. The positive ions are detected with a Galileo 4770 high-current Channeltron with a measured gain of 3×10^6 at -3 kV. The current from the multiplier is detected with a Keithley 18000-20 picoammeter with programmable ranges of $10 \text{ V}/10^{-10} \text{ A}$ to $10 \text{ V}/10^{-3} \text{ A}$.

The components of the mass spectrometer are enclosed in three differentially pumped stainless steel chambers, each pumped by an oil diffusion pump with water-cooled baffle (see Figure 5). Normal operating pressures in the three chambers, as indicated by ion gauges, are source chamber: 2×10^{-7} torr for EI and 6×10^{-4} torr for CI; center chamber: 2×10^{-6} torr (no collision gas); detector chamber: 2×10^{-6} torr. Collision gas pressures from 2×10^{-6} torr to 1×10^{-2} torr are possible.

The entire vacuum system is interlocked to provide fail-safe operation and permit computerized cycling of the vacuum system. Foreline pressures, coolant water flow, electric current through the pumps, pneumatic pressure, and valve positions are all monitored and used to control the proper sequencing of all pumps, electropneumatic valves, and electronics.

Data acquisition from the system is currently either manual (strip chart recorder or oscilloscope), or automated with an Intel SDK-85 microprocessor, CRT terminal, and floppy disc. A multiple microprocessor system employing the Intel 8085 is currently under development for data acquisition and intelligent

control of the instrument. The entire system has been designed for computer control, including the mass selection in both mass filters, the selection of mass filter or total-ion mode, the RF voltage on all three quadrupoles, the control of collision and CI gases, and the vacuum interlock. The capabilities of the triple quadrupole system for selected ion fragmentation will be significantly enhanced under complete computer control.

PERFORMANCE OF INSTRUMENT

The use of quadrupoles as mass filters and as the CID chamber has provided the anticipated excellent selectivity and sensitivity. Selectivity is achieved by tandem mass separation up to mass 1000 with a resolution of better than 1 amu. The high sensitivity (detection limit of 10^{-15} mole) results from the very efficient low-energy CID process and the high transmission of each component along the ion path.

Resolution

The ultimate resolution of the quadrupoles is approximately 1 part in 1500, as determined by measuring peak width at half height. As an example of the resolving power, the N^+ / CH_2^+ doublet at 14 amu can be resolved (50% valley), which requires a resolution of 1 part in 1100. The mass filters can be operated in two modes: constant resolution and resolution proportional to mass. At constant resolution (e.g., 1 part in 1000 over entire mass range) the relative abundance of the ions in a mass spectrum closely resembles that observed with double-focusing mass spectrometers. With resolution proportional to mass (e.g., 1 part in 100 at mass 50, 1 part in 1000 at mass 500), the intensity of the low mass

peaks is enhanced. The quadrupoles are typically operated with unit mass resolution (1% valley) over the entire mass range. The peak broadening due to kinetic energy loss on fragmentation that is observed with MIKES instruments does not occur with the quadrupole mass filter.

CID Efficiency

The high sensitivity of the triple quadrupole system is a result of the high efficiency of each component. The ion source and lenses produce approximately 1 ion for every 2×10^5 molecules. The mass filters have a transmission efficiency of approximately 60% in RF-only mode and 10% in mass filter mode with resolution of 1 part in 200. The center quadrupole has virtually 100% transmission. Even more important is the efficiency of the CID process which occurs in the center quadrupole. In an earlier investigation of the low-energy CID process in a triple quadrupole system (2), three expressions were developed to describe the efficiency. The collection efficiency is the ratio of the ion flux at the exit of the quadrupole to that at the entrance. With no collision gas present, there is 100% collection. At 2×10^{-4} torr collision gas pressure, the collection efficiency ranges from 50% for light ions like CH_4^+ up to 75% for heavier ions which are less prone to scatter. The strong focusing of the quadrupole field minimizes scattering losses. The fragmentation efficiency is the fraction of the ion flux at the exit of the center quad that is due to fragment ions. At 2×10^{-4} torr, fragmentation efficiency range from 15% to 65% for various compounds (2). As the collision gas pressure is increased, the fragmentation efficiency for all compounds approaches 100% due to multiple collisions, but the collection efficiency decreases due to scattering. The overall CID efficiency, which is the product of the collection and fragmentation efficiencies, exhibits a maximum

at some intermediate pressure. The collection efficiency as a function of collision gas pressure for the dissociation of CH_4^+ from methane is shown in Figure 6. The fragmentation efficiencies for the production of the CH_3^+ and CH_2^+ ions are also shown.

Several factors other than collision gas pressure can affect the efficiency of the CID process (2). The larger the molecular diameter of the collision gas, the more efficient the CID. Ion axial energy and ion internal energy also affect the CID process. A more detailed study of these effects is in progress (11).

Sensitivity

The overall sensitivity of the instrument can be estimated from the product of the efficiencies of the individual processes. The source efficiency and the transmission through the three quads (without collision) are 2×10^{-5} and 10^{-2} respectively. The fragmentation efficiency is a function of the ion and fragment selected, but from Figure 6 it is seen to be about 0.1 for $\text{CH}_4^+ \rightarrow \text{CH}_3^+$. The overall efficiency is 2×10^{-8} , i.e., two CH_3^+ ions reach the detector per 10^8 CH_4 molecules passing through the source. The detection system can measure the current due to one ion per second which is an average current of 5×10^{-13} A. For methane, then, a current of 4×10^{-10} A will be produced from a sample flux of 1 pg per second.

The ultimate detection limit depends on the system sensitivity, the chemical and electrical noise levels, and the lowest measurable signal level. The electrical noise in the system is typically 3×10^{-13} A. The two stages of mass separation often make it possible to reduce chemical noise (ions detected from other than the desired reaction) to well below the 10^{-13} A

level. In such a case, at the extreme sensitivity limit, the peak height is quantized by the integer number of ions which reach the detector during the scanning time of the peak. The detection of 4 ions would give an S/N of 2 and, for methane, would require, 6 fg of sample. The detection limit for methane has been determined experimentally to be 16 femtograms by measuring a sample of 10 ppm CH_4 in N_2 at a sample flux of 20 femtograms per sec of CH_4 . The large excess of N_2 is required to increase the ion source pressure so that it can be accurately measured and the sample flux calculated. The selectivity of monitoring the $\text{CH}_4^+ \rightarrow \text{CH}_3^+$ reaction has effected a two order of magnitude improvement in detection limit compared to that obtained by simply monitoring the CH_4^+ , CH_3^+ , or CH_2^+ ions from electron impact. This improvement is due to the elimination of the chemical noise introduced by background $^{14}\text{N}^+$, $^{15}\text{N}^+$ and $^{16}\text{O}^+$ peaks.

The selected ion fragmentation capability of the instrument produces only a small loss in transmission and sensitivity, and produces a significant gain in selectivity. Indeed, in the normal case where the system is limited by chemical rather than electrical noise (3), a substantial improvement in detection limit can be achieved as was observed for methane. The detection limit of approximately 10^{-15} mole is made possible by the high efficiency of every component of the system.

The detection limit for a higher mass organic compound, nitrobenzene, has also been determined experimentally. The transition $\text{NO}_2\text{C}_6\text{H}_5^+ \rightarrow \text{C}_6\text{H}_5^+$ was monitored at unit mass resolution in both mass filters, with the parent

ion produced by electron impact on a sample of 10 ppm nitrobenzene in N_2 . A detection limit of 120 femtograms ($S/N = 2$) was obtained with a sample flux of 200 femtograms/second. In comparison, for the MIKES technique, Cooks has estimated a detection limit of 10 pg for the $140^+ \rightarrow 123^+$ transition of protonated nitrophenol ions produced by CI (22). Although consumption of only femtograms is required for recording the single reaction, actual sample size is significantly larger than this and is dependent on the sample inlet used. Total consumption of a sample introduced by direct probe should make it possible to detect quantities of individual components at close to these detection limits.

CONCLUSIONS

The CID process performed in the strong focusing field of an RF-only quadrupole is efficient and effective in producing characteristic spectra of selected ions. The kinetic energy independence of the mass resolution is ideal for collision product analysis. The lack of interdependence in the control of the two mass filters makes it easy to implement the various analytical modes.

The system can be used to detect species present in a mixture including isomers without prior separation at the 10^{-15} mole level. The capability to select a desired initial mass and specific collision product mass reduces chemical noise dramatically. For structure elucidation applications, the spectra of selected functional moieties in the molecule may be obtained. Among the many other promising applications of the selected ion fragmentation technique is the analysis of isotopically labelled samples, in which the first mass filter can eliminate interferences from molecules that are not completely labelled.

ACKNOWLEDGEMENT

We wish to acknowledge the work of the MSU Chemistry Department Machine Shop headed by Russ Geyer, and master machinist Len Eisele who constructed much of the instrument. We would also like to express our gratitude to Kaz Latven, John Chakel and Fritz Allen who helped to get the instrument functioning and demonstrate its application. Finally, we would like to acknowledge the invaluable time spent in the laboratory of Jim Morrison at La Trobe University and helpful discussions with Graham Cooks and Chuck Sweeley.

FIGURE CAPTIONS

- Figure 1. Conceptual diagram of the triple quadrupole mass spectrometer showing each component and its function.
- Figure 2. Three-dimensional fragmentation map for cyclohexane.
- Figure 3. Comparison of CID spectra of selected ions in the EI spectrum of a five component mixture with reference CID spectra from pure components.
- Figure 4. Structure elucidation of 43^+ functional moiety by interpretation of CID spectrum and comparison with reference CID spectra.
- Figure 5. Scale drawing (top view) of triple quadrupole mass spectrometer.
- Figure 6. Effect of collision gas (N_2) pressure on CID efficiency for methane CH_4^+ at ion axial energy of 10eV.

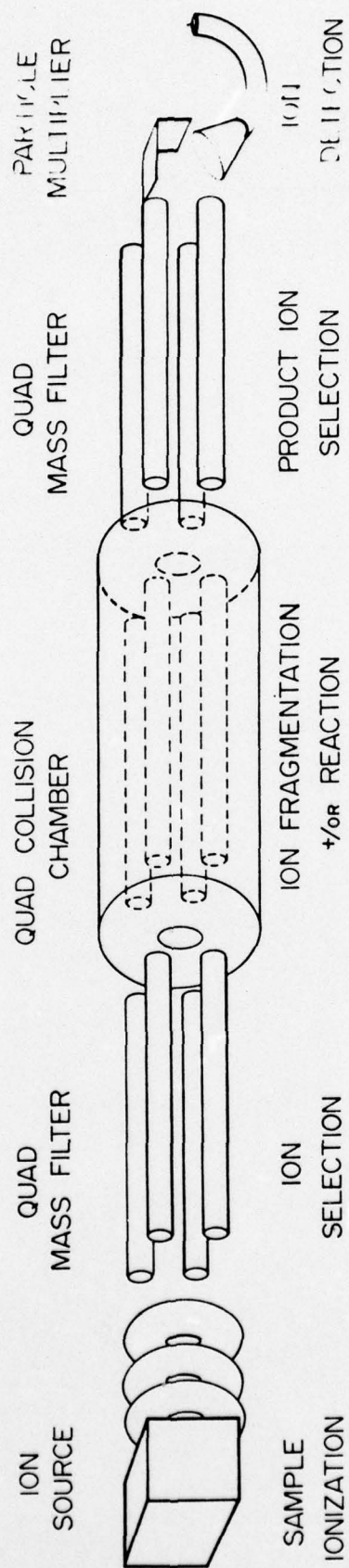


FIG. 1 - Yost, Enke, Triple Quadrupole Mass Spectrometry . . .

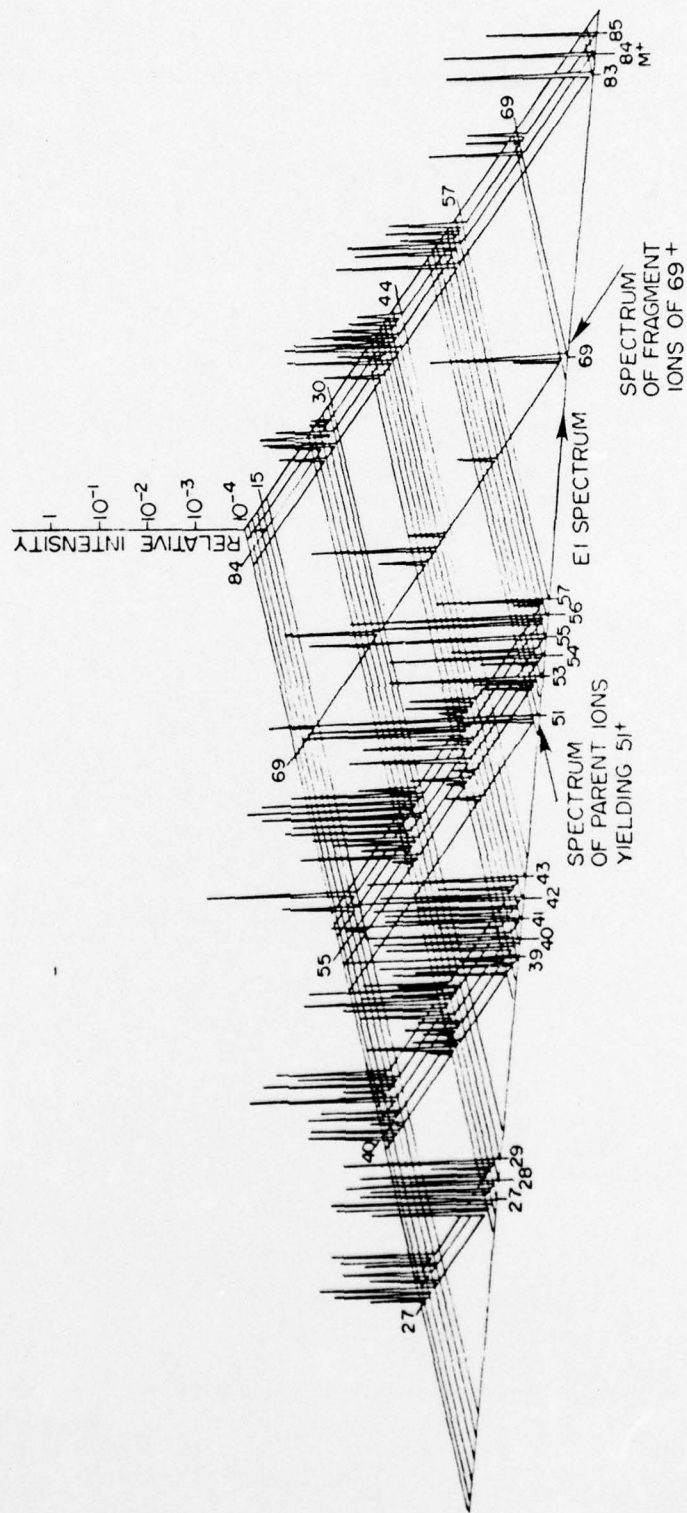


FIG. 2 - Yost, Enke, Triple Quadrangle Mass Spectrometry . . .

ION FRAGMENTATION SPECTRA OF SELECTED IONS

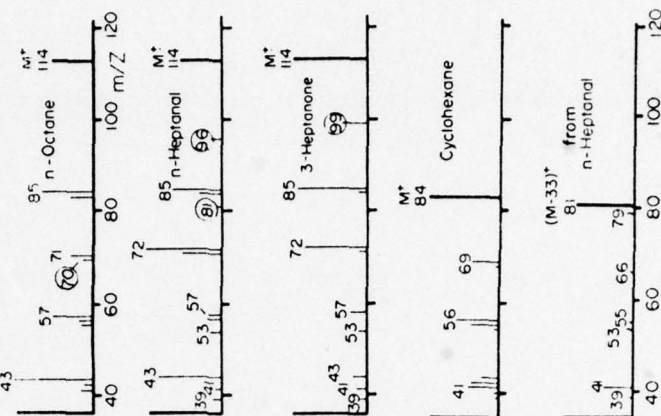
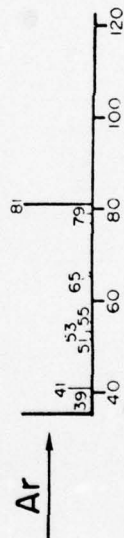
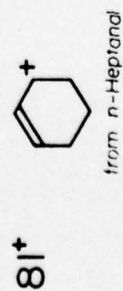
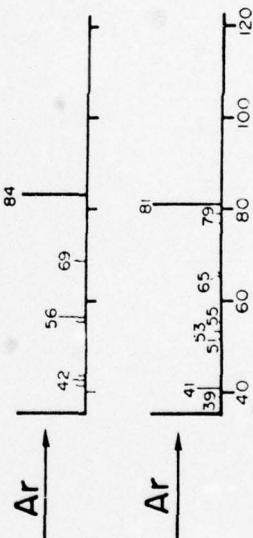
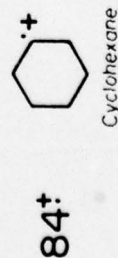
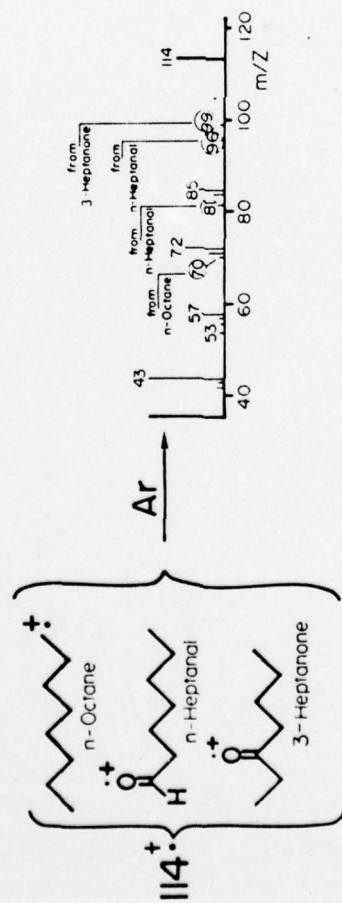


FIG. 3 - Yost, Enke, Triple Quadrupole Mass Spectrometry . . .

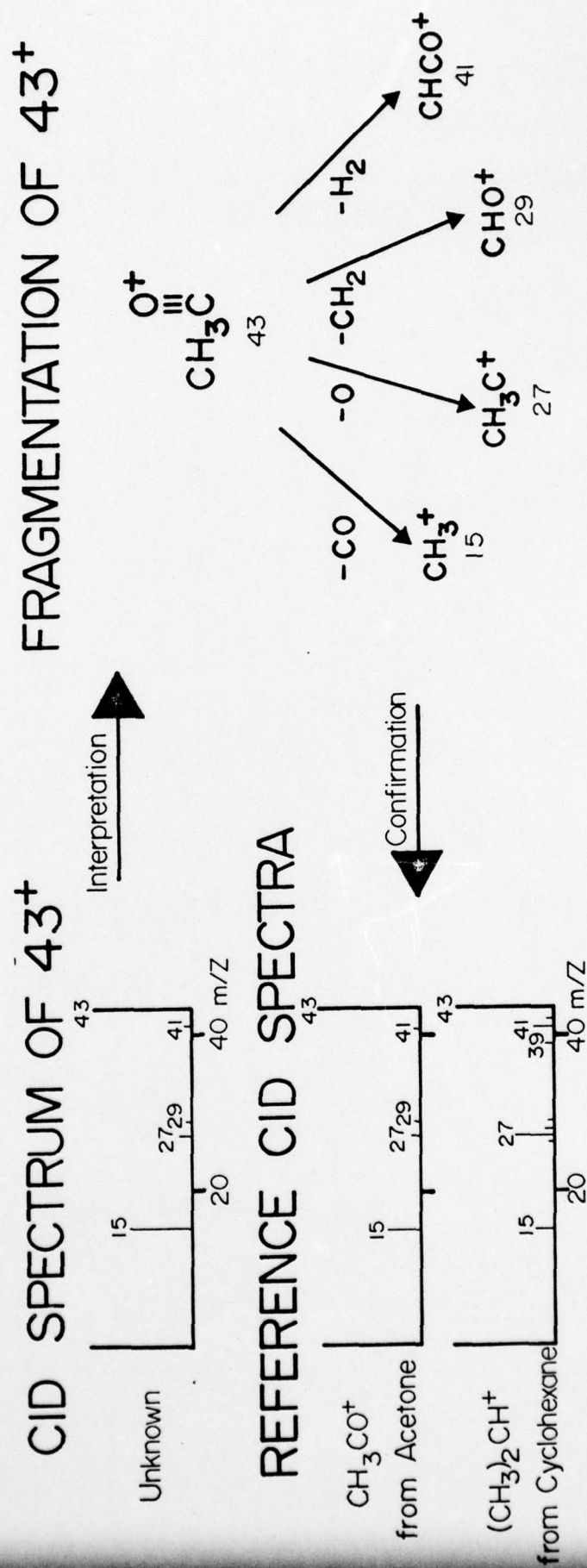


FIG. 4 - Yost, Enke, Triple Quadrupole Mass Spectrometry . . .

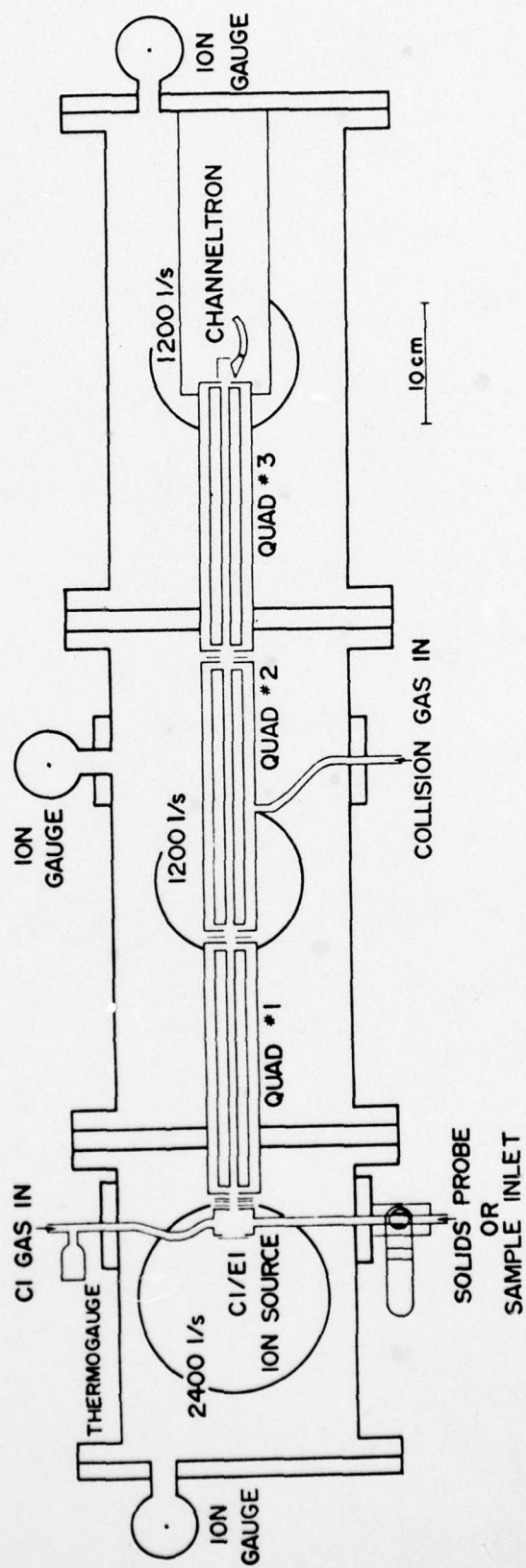


FIG. 5 - Yost, Enke, Triple Quadrupole Mass Spectrometry . . .

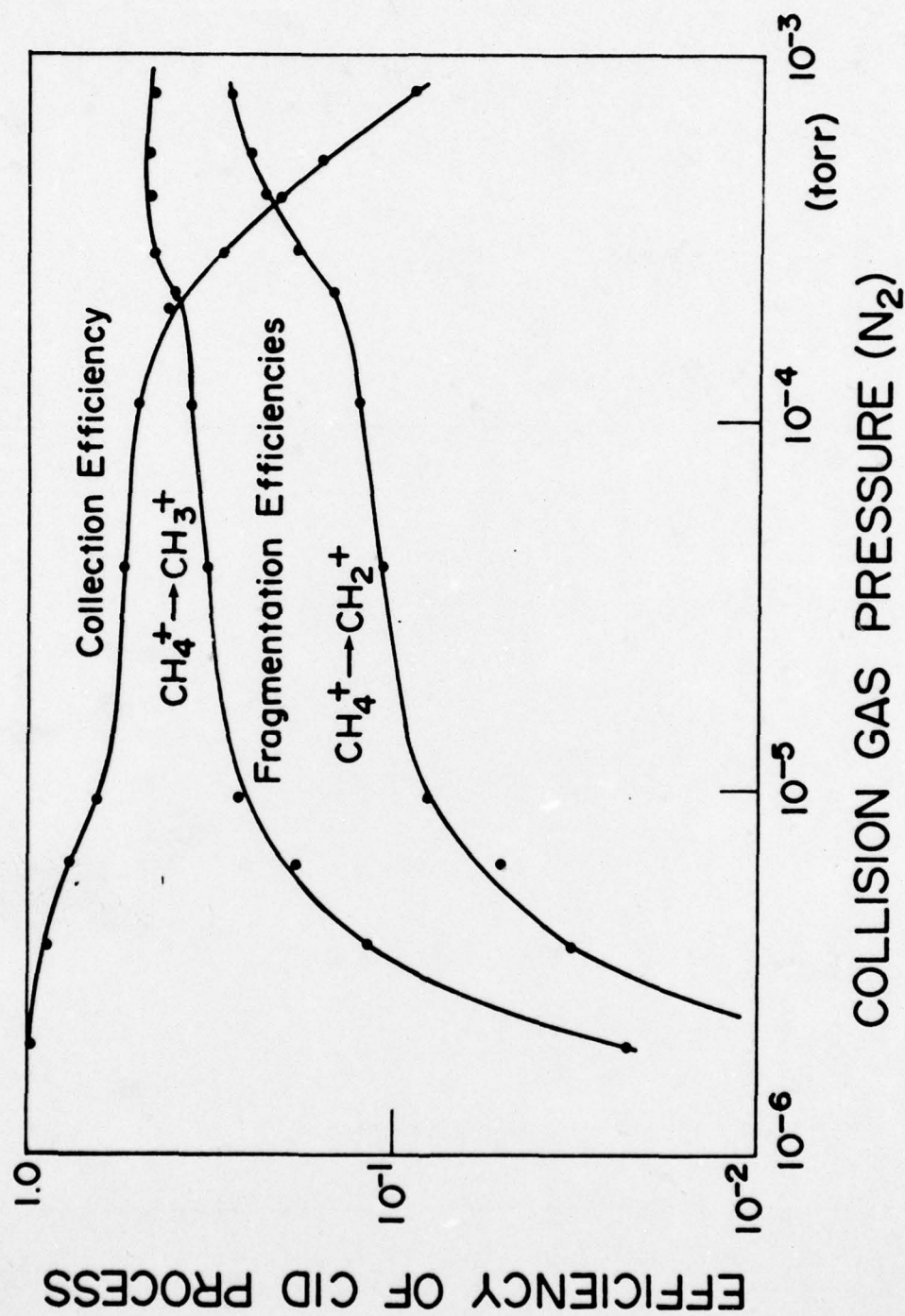


FIG. 6 - Yost, Enke, Triple Quadrupole Mass Spectrometry . . .

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