

Fast Multidimensional (3D and 4D) MS² and MS³ Scans in a High-Transmission Pentaquadrupole Mass Spectrometer

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A high-transmission Extrel pentaquadrupole mass spectrometer was interfaced to an IBM-compatible microcomputer, and a variety of object-oriented programs in the Microsoft Windows operating system were developed to operate and to increase the versatility of the instrument. A selective prescan procedure and the complete control of all three mass-scanning quadrupoles made possible very fast acquisition of several types of three- and four-dimensional MS² and MS³ spectra, while the high transmission of the quadrupoles conferred excellent signal-to-noise levels to both MS² and MS³ spectra. By performing an unrestricted third-order (MS³) experiment through scanning of the three mass-analyzer quadrupoles, an entire MS³ data domain was acquired, and the results were collected in the first 4D MS³ mass spectrum. Data projection and data extraction procedures were applied to the 4D spectrum, each of which yielded spectra that provide very specific analytical information. The applicabilities of this and several other multidimensional mass scans were further demonstrated, particularly toward the study of gas phase ion chemistry processes. A consecutive MS³ neutral gain/neutral loss scan was for the first time applied and proved to be very selective for the detection of acylium ions in the gas phase. The application of a 3D MS² scan, applied in conjunction with the membrane introduction mass spectrometry technique, for fast and simultaneous qualitative, quantitative, and structural analyses of volatile organic compounds in water was also demonstrated.

Tandem or double-stage mass spectrometry (MS²) is a very valuable analytical method that has been performed in a variety of mass spectrometers.¹ Such instruments are mainly divided in two categories: the multiple-analyzer and the ion trap types of mass spectrometers, each of which shows advantages in performing some specific tasks.^{1e} The multiple-analyzer instruments include triple-quadrupoles (QqQ), sectors such as EBEB, and

hybrid instruments such as EBQ, which allow the performance of tandem-in-space MS² experiments.^{1c} On the other hand, the single-analyzer quadrupole ion traps (ITMS) and ion cyclotron resonance (ICR) mass spectrometers perform tandem-in-time experiments, which can employ various, instrumentally unlimited stages of mass analysis (MSⁿ).^{1f} Perhaps the most used mass spectrometer in the MS² field has been the triple-quadrupole,^{1c} which allows the efficient performance of the whole set of MS² experiments, while its tandem-in-space mode very much simplifies the acquisition of multidimensional spectra.² A more sophisticated implementation of multiple-quadrupole instruments is the recently introduced pentaquadrupole mass spectrometer (QqQqQ).³ Pentaquadrupoles employ an ion source, two rf-only reaction quadrupoles (q2 and q4), and three mass-analyzing quadrupoles (Q1, Q3, and Q5). Their on-line arrangement (tandem-in-space) allows the study of reactions that occur in sequence in the two separate reaction regions by using three stages of mass analysis. Given, therefore, the ability to mass-analyze ions before and after each of the reaction regions, a powerful and diverse set of MS³ experiments are available. These experiments allow access to very specific types of information about gas phase reactions, such as their ionic intermediates, the connecting processes, and the structures of the reaction products, with significant advantages in chemical selectivity.^{4,5} A characteristic example is provided by

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the sequential dissociation of peptide ions, which can provide detailed information about their sequencing.^{1e,4} The pentaquadrupole is also particularly useful for multiple-stage mass spectrometric experiments, because it allows all types of MS³ experiments² to be accessed, and in allowing either ion/molecule reactions or collision-induced dissociation (CID) to be performed in either of the two separated reaction regions. Also, by scanning sequentially two or all three of the mass-analyzing quadrupoles, a variety of three-dimensional (3D) and four-dimensional (4D) mass spectra² can be obtained, each of them providing specific and detailed information about the processes under investigation.

The systematic basis of multidimensional mass spectrometry was recently outlined.² In this study, the authors developed a complete methodology for representing, categorizing, and understanding multidimensional mass scan modes, several of which they implemented both in a hybrid (BEqQ) and in a pentaquadrupole mass spectrometer. The utility of these multidimensional mass scans to the study of several ion dissociation processes was also demonstrated. More recently, a variety of other applications of several pentaquadrupole MS³ mass scans have been demonstrated, especially toward the investigation of gas phase ion chemistry processes.⁵

The main drawbacks of pentaquadrupole mass spectrometers for performing MS³ scans are, however, the lower overall ion transmission and the excessive time that is consumed in the data acquisition process. Ion transmission is diminished by the three stages of ion mass analysis and by the ion current depletion that occurs in the two reaction regions. These limitations call for the application of time-consuming data averaging and spectrum accumulation routines. For the 3D scans,^{5c} quite long acquisition times, normally on the order of a couple of hours, have been required for the acquisition of the whole domain of data. This paper shows, however, that these disadvantages can be very satisfactorily surpassed by using a high-transmission pentaquadrupole mass spectrometer in which very fast multidimensional (3D and 4D) mass scans can be performed. Very satisfactory transmissions in the MS³ modes are obtained by the use of the high-transmission Extrel 3/4-in. quadrupoles, whereas adequate computer control and software development, including a selective prescan procedure, allow very fast acquisition of the complete domain of data for several 3D and a 4D mass spectra. New applications of these scans are also demonstrated.

HARDWARE IMPLEMENTATION

Figure 1 shows the block diagram of the equipment. The quadrupoles Q1, Q3, and Q5 are mass analyzers, while q2 and q4 are rf-only quadrupoles used as collision or reaction chambers. This instrument as well as the electronic rf/dc generator was assembled by Extrel Corp. (Pittsburgh, PA). All 3/4-in. rod diameter scanning quadrupoles (Q1, Q3, and Q5) work at 880 kHz, with a mass range of 1–1000 u. The ion source with interchangeable ion volumes allows the performance of both electron impact (EI) and chemical ionization (CI). The detector system consists of a Galileo electron multiplier detector (EM) with a conversion dynode that allows the detection of both positive and negative ions. The mass spectrometer was interfaced with an IBM-compatible microcomputer equipped with a 486DX 50-MHz microprocessor, 20 MB of random access memory, a SVGA color monitor, and a 540-MB hard disk.

An AT-MIO-16X card (National Instruments) controls the main functions of the instrument. This card is provided with one 16-

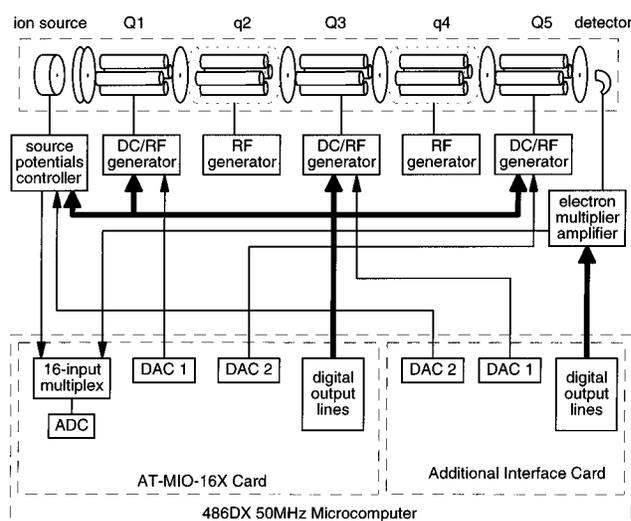


Figure 1. Block diagram of the Extrel pentaquadrupole mass spectrometer. The arrows show the flow of the information between the microcomputer and the spectrometer. The internal dashed rectangles represent the interface cards, while the microcomputer is represented by the external dashed rectangle.

bit analog-to-digital converter (ADC) that contains 16 single-ended or eight differential channels capable of acquiring data at 100 kHz; two independent 16-bit digital-to-analog converters (DACs); eight digital input/output lines; and three independent 16-bit counter/timers. The DACs are used to set the m/z values of both Q1 and Q5. The ADC is used to acquire the ion abundance and to monitor ion source potentials and EM high voltage. Three digital output lines are used to switch Q1, Q3, and Q5 quadrupoles between the mass-analyzing and rf-only modes.

To achieve full control of all three scanning quadrupoles, an additional card based on a DAC725 dual 16-bit DAC from Burr-Brown was developed for Q3 control. The remaining DAC channel was used to control the ionization energy. The circuit also contains an 8-bit output latch from which two lines are used to set the gain of the EM amplifier.

SOFTWARE

The basic routines that control the AT-MIO-16X card were supplied by the manufacturer. The routines for the additional card as well as the programs for data acquisition and treatment were developed in Turbo Pascal 1.5 for Windows (Borland Inc.). Because of the interfacing complexity, object-oriented programming (OOP)⁶ was chosen, which allows one to organize the basic structures and then expand the system. Several programs were developed to acquire 2D, 3D, and 4D spectra. All the signals were filtered by the application of a moving median procedure.⁷ To speed up the acquisition process and also to save memory, the fast scanning method described in the following text was implemented. The first mass-analyzer quadrupole (Q1)⁸ is scanned with 1-u increments while the others are kept in the rf-only mode. A peak is recorded for each integer mass value where the signal-to-noise ratio of the ion abundance exceeds the limit of detection.

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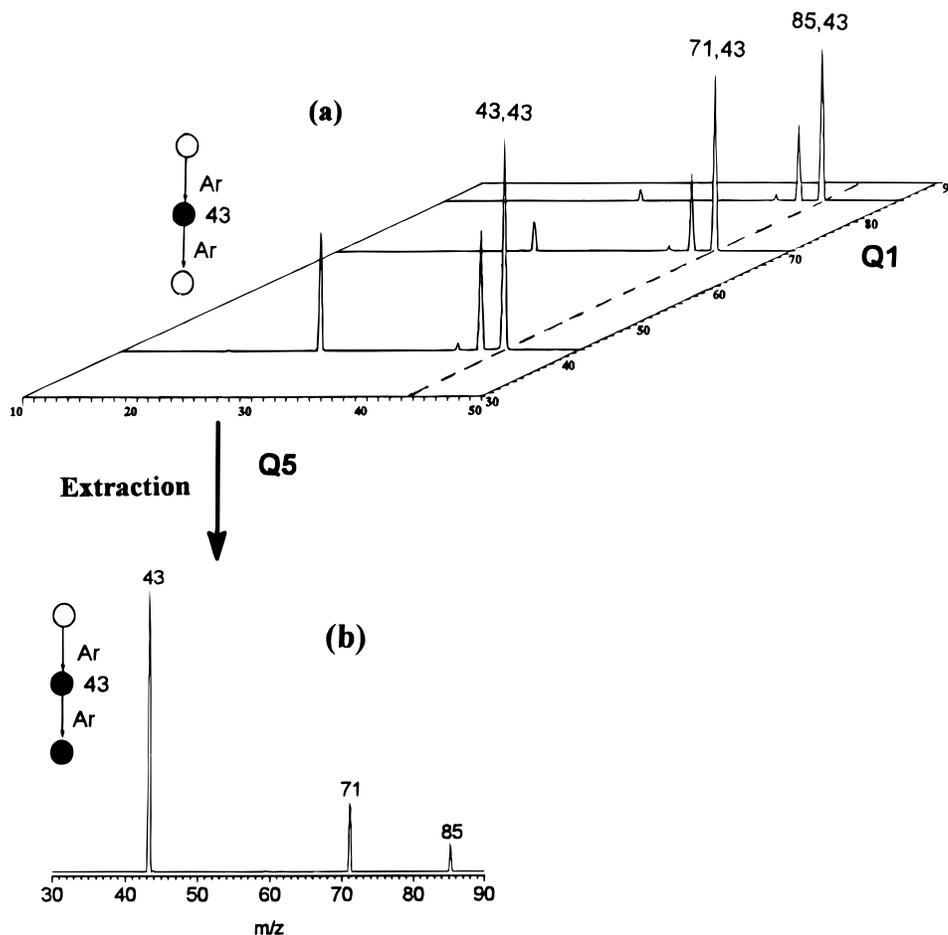


Figure 2. (a) Three-dimensional MS³ familial scan for *n*-nonane, acquired by selecting the *m/z* 43 ion as the intermediate. The Q1 angled axis displays the parent of *m/z* 43, while the Q5 horizontal axis displays the 10-eV CID products of the *m/z* 43 ions generated specifically from each of its parents. (b) Extracted 2D MS³ sequential parent spectrum, showing the parent ions (P) which undergo the dissociation sequence P → *m/z* 43 → *m/z* 27.

In this manner, a conventional mass spectrum of the sample is acquired. In a second step, the peaks with intensities above 10 standard deviations are explored by the other quadrupoles. The abundance is optimized by local mass-scanning in a ± 0.2 -u window to find out the maximum intensity position. The quadrupole is then fixed at this value and the scanning process is repeated for the next quadrupole. For the 4D scans, the process is carried out for Q1, Q3, and Q5, but the step of optimizing the abundances is suppressed for Q5. This method is time and memory saving because a quadrupole is scanned only when a large peak is found in the preceding one. The actual time and memory consumption depends on each case, but usually only a few minutes are necessary for the acquisition of a full 4D spectrum.

APPLICATIONS

A 3D Familial Spectrum.⁹ Figure 2a shows a 3D MS³ familial spectrum obtained with the pentaquadrupole. This spectrum is related to the first scan of this type that was acquired in a hybrid BEqQ mass spectrometer² and was obtained by mass-selecting the *m/z* 43 fragment ion of *n*-nonane in Q3 and performing 10-eV CID with argon in both q2 and q4 while scanning sequentially both Q1 and Q5. Instrumentally, this

scanning process was accomplished by stepping Q1 one mass at a time while Q5 was scanned along the entire mass range of interest at each setting of Q1. As seen in Figure 2a, the prescan procedure applied prior to the acquisition of the 3D spectrum identified Q1 parent ions at *m/z* 43, 71, and 85. Therefore, Q5 was scanned only when Q1 was set exactly at these preselected masses. Fast data acquisition, on the order of a few seconds, was therefore accomplished. The high overall transmission of the instrument¹⁰ also confers an excellent signal-to-noise ratio to the spectrum, which speeds up the data acquisition by minimizing the need for data averaging and by eliminating the need for spectrum accumulation.

This scan mode leads, therefore, to the acquisition of a 3D mass spectrum in which all the parents (*m/z* 43, 71, and 85) of the Q3 mass-selected *m/z* 43 ion are displayed along the angled Q1 axis. The horizontal Q5 axis, on the other hand, displays all the fragments of the *m/z* 43 ions generated from each specific Q1 mass-selected parent. As expected from the dissociation chemistry displayed by *n*-alkanes,¹¹ the similar set of product ions (*m/z* 41, 39 and 27) indicate that all parents generate the same

(9) The name "familial scan" has been chosen to describe the experiment since the relationship of all products and all parents to a particular intermediate ion is obtained; see ref 2.

(10) As an example of the high transmission of the Extrel pentaquadrupole mass spectrometer, 15–20% overall transmission was obtained in MS³ experiments in which the dissociation sequence *m/z* 219 → *m/z* 131 → *m/z* 69 for the FC-43 standard was induced by collisions with argon in both q2 and q4.

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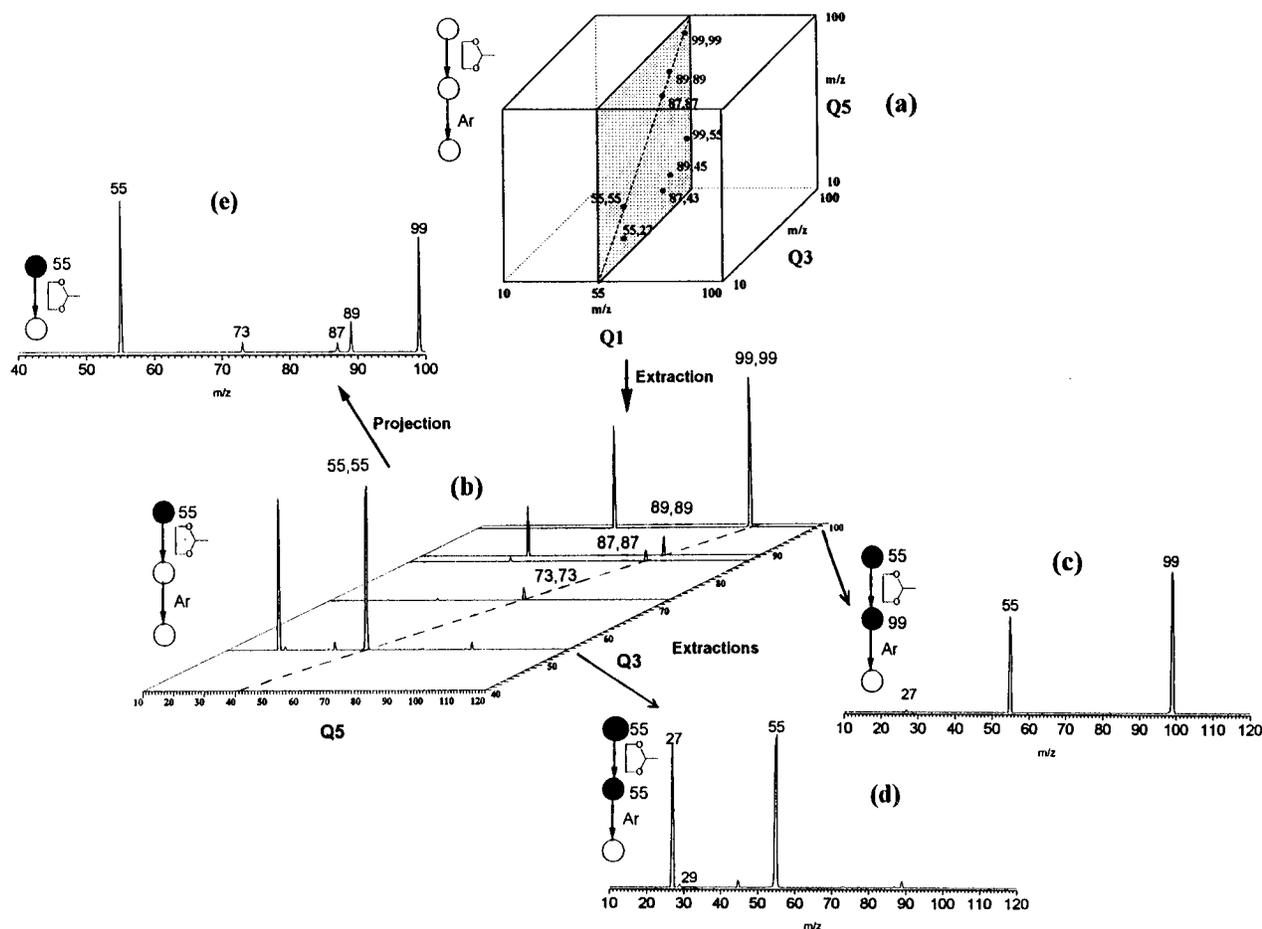


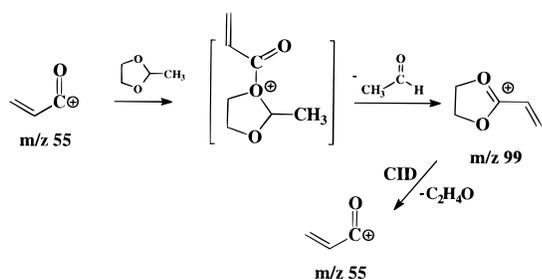
Figure 3. (a) First 4D MS³ spectrum (abundance axis not included) obtained by sequential scanning of all three mass-analyzer quadrupoles, which contains the entire MS³ data domain for cyclopentanone ions. (b) The 3D MS³ spectrum, which was extracted from the 4D spectrum along the hatched $m/z(Q1)$ 55 plane. All the reaction products of m/z 55 with 2-methyl-1,3-dioxolane are displayed along the diagonal dashed line, in which equal masses in both Q3 and Q5 are selected, whereas their corresponding 15-eV CID fragments are displayed along the horizontal Q5 axis. Extracted 2D MS³ sequential product spectra of (c) the m/z 99 reaction product and (d) the m/z 55 surviving reactant ion. (e) Reconstructed (by projection toward the Q3 axis) 2D MS² product spectrum of the m/z 55 ion.

m/z 43 ion with the $C_3H_7^+$ composition. Figure 2b shows a lower-dimensional (2D) MS³ spectrum that can be extracted and reconstructed (by reflection of the peaks from the Q5 to the Q1 axis) from the 3D plot. This spectrum corresponds to a MS³ sequential parent scan² and displays all the n -nonane parent ions that dissociate to m/z 43 ions, which in turn dissociate by methane loss (16 u) to form m/z 27 fragments. Note that loss of methane is characteristic of m/z 43 ions with the $C_3H_7^+$ composition.

The First Four-Dimensional MS³ Spectrum. Figure 3a presents schematically the first example of a 4D mass spectrum, which contains an entire MS³ data domain,² from which several lower-dimensional spectra can be obtained. The 4D spectrum was obtained for cyclopentanone in only a few minutes of acquisition time. The computer control allows the selection one at a time of all of the source-generated cyclopentanone ions in Q1, which were then submitted to near-zero-eV ion/molecule reactions with 2-methyl-1,3-dioxolane in q2. The product ions formed in such reactions were mass-selected, again one at a time in Q3, and subjected to 15-eV CID with argon in q4, while Q5 recorded each individual dissociation spectrum. The 4D data presented in Figure 3a (of course, the fourth abundance axis cannot be shown) contain, therefore, the ion/molecule products and the relative abundances of all the cyclopentanone ions, each directly associated with their dissociation products. Evidently, more specific information and

a partial, but better, visualization of the 4D data can be obtained by extracting data of lower dimensionality, as exemplified in Figure 3b. This 3D spectrum was obtained by extracting the data contained in the $m/z(Q1)$ 55 plane and, therefore, presents all data that are related specifically to the m/z 55 Q1 mass-selected ion. This corresponds to a scan mode in which the m/z 55 ion is mass-selected in Q1, and both Q3 and Q5 are sequentially scanned. A detailed and complete view of the whole ion/molecule process for the m/z 55 ion is therefore presented in this 3D spectrum. Across the diagonal line in Figure 3a, in which equal masses in both Q3 and Q5 are selected, the surviving reactant ion (m/z 55) and all of its reaction products with 2-methyl-1,3-dioxolane are displayed (m/z 73, 87, 89, and 99). On the other hand, the CID fragments of each individually selected product can be seen across the Q5 axis. The m/z 55 ion has the α - β unsaturated acylium ion structure $CH_2=CHC^+=O$ ¹¹ and it reacts extensively with 2-methyl-1,3-dioxolane by a formal oxirane addition (44 u) reaction. This reaction is structurally diagnostic for acylium ions^{5e} and yields a 1,3-dioxolanylium ion at m/z 99 (Scheme 1). As seen in Figure 3b, the m/z 99 product fragments extensively by C_2H_4O neutral loss (44 u), a process that most likely regenerates the reactant ion at m/z 55. Figure 3b also shows that protonated 2-methyl-1,3-dioxolane (m/z 89) fragments extensively to m/z 45, while the 2-methyl-1,3-dioxolanylium ion at m/z 87,

Scheme 1



formed most likely by hydride transfer,¹² fragments almost exclusively by $\text{C}_2\text{H}_4\text{O}$ loss to m/z 43. It is worth noting that the identity of the reactant ion also can be investigated by the data presented in the 3D spectrum. The m/z 55 ion is shown to fragment extensively to m/z 27 by neutral CO loss, exactly as expected from its α - β unsaturated acylium ion structure $\text{CH}_2=\text{CHC}^+=\text{O}$.¹¹

Further extraction from the 3D spectrum along the Q5 axis (fixed Q3 masses) produces 2D MS³ sequential product spectra, as exemplified for the m/z 99 product ion in Figure 3c and for the reactant ion in Figure 3d. These spectra display separately in 2D plots the fragments of each selected ion/molecule reaction product and additionally those of the reactant ion, which can be used for structural assignments.

Projection of the 3D spectrum toward the Q5 axis allows one to reconstruct the 2D MS² product spectrum of the m/z 55 ion (Figure 3e). This is accomplished by adding to the abundances of the surviving ions those of their corresponding fragments. In

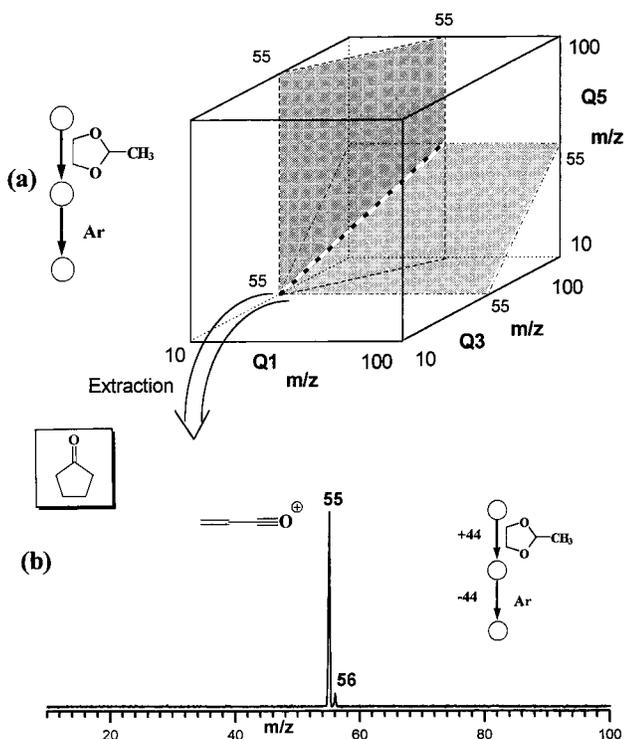


Figure 4. (a) 4D MS³ spectrum containing the entire MS³ data domain for cyclopentanone ions, showing the two planes described by the equations $m/z(Q3) = m/z(Q1) + 44$ and $m/z(Q5) = m/z(Q3) - 44$. (b) MS³ consecutive 44-u neutral gain/neutral loss (NGNL) spectrum, which was extracted from the 4D spectrum along the line defined by the intersection between the two planes. Only the m/z 55 acylium ion (and its m/z 56 isotopes) responds to the 44-u NGNL test.

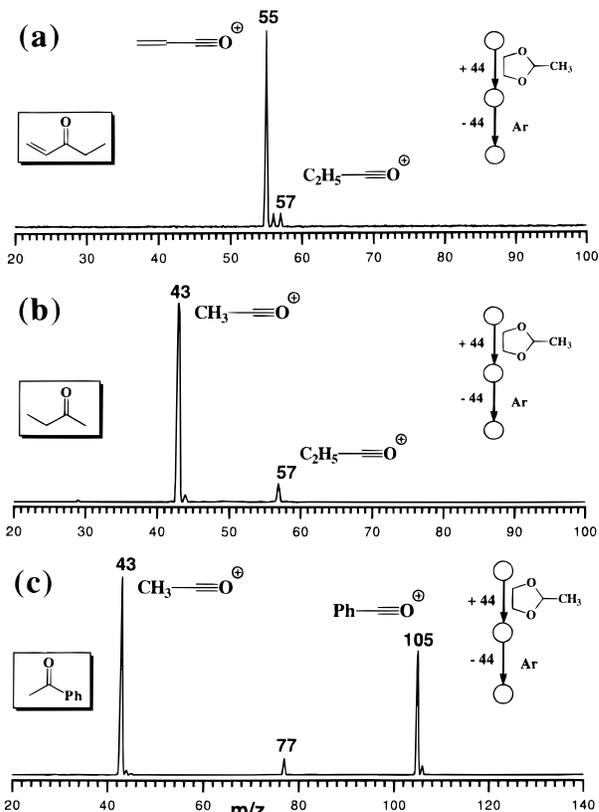


Figure 5. MS³ consecutive 44-u neutral gain/neutral loss (NGNL) spectra applied for the ions produced from (a) ethyl vinyl ketone, (b) 2-butanone, and (c) acetophenone. The spectra were obtained by simultaneous scanning of all three mass quadrupoles. Note that only the acylium ions respond to the 44-u NGNL test.

the reconstructed spectrum, the effect of depletion of the relative abundance of the product ions caused by fragmentation in q4 is canceled out; therefore, the corrected yields of the ion/molecule products are obtained. The reconstructed abundances should therefore be similar to those obtained if a direct MS² ion/molecule reaction product spectrum is recorded, as is, indeed, observed (spectrum not shown).

Figure 4 shows another 2D MS³ spectrum that was extracted from the 4D spectrum. Data were extracted along the line defined as the intersection between the two planes described by the equations $m/z(Q3) = m/z(Q1) + 44$ and $m/z(Q5) = m/z(Q3) - 44$ (Figure 4a). The resulting spectrum (Figure 4b) corresponds to the first MS³ spectrum acquired by applying the consecutive neutral gain/neutral loss (NGNL) scan mode, which is a derivative of the consecutive neutral loss scan that has already been implemented.² Such a spectrum is therefore expected to display only the cyclopentanone ions which react with 2-methyldioxolane in q2, yielding products corresponding to a 44-u mass gain, and which further fragment upon collision with argon in q4 also by loss of 44 u. As seen in Figure 3b, the acylium ion at m/z 55 (and a mixture of mainly its ¹³C and ²H isotopes at m/z 56)

(12) Proton transfer from acylium ions to 2-methyl-1,3-dioxolane has been previously assigned to yield to corresponding protonated molecule at m/z 89 and their loss of H_2 , CH_4 , and acetaldehyde fragments at m/z 87, 73, and 45, respectively; see ref 5e. However, the MS³ spectrum of m/z 89 (Figure 3b) has shown that it fragments exclusively to m/z 45. Thus, the major m/z 87 ion is best rationalized as being originated by hydride transfer. Charge-exchange followed by rapid hydrogen atom loss of the ionized dioxolane is also an alternative, although charge-exchange is somewhat unusual for closed-shell cations.

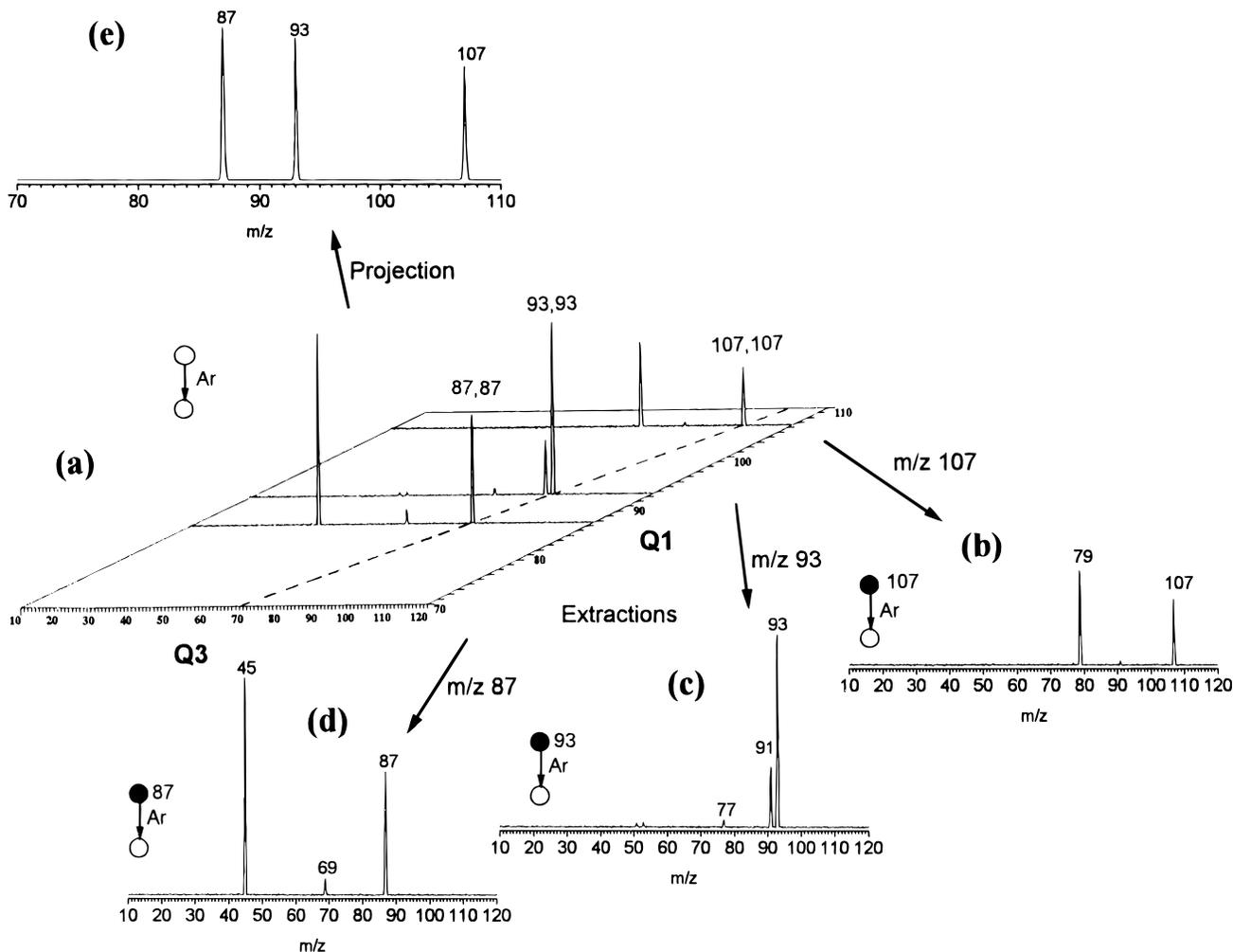


Figure 6. (a) Three-dimensional spectrum that shows the entire MS² data domain of an aqueous solution of 2-pentanone, toluene, and benzaldehyde introduced by MIMS, ionized by methane Cl, and subjected in q2 to 15-eV collisions with argon. The Q1 mass-selected protonated molecules are displayed along the diagonal dashed line, whereas their corresponding dissociation products are displayed along the horizontal Q3 axis. Extracted MS² 2D sequential product spectrum of (b) protonated 2-pentanone (m/z 87), (c) protonated toluene (m/z 93), and (d) protonated benzaldehyde (m/z 107). (e) Reconstructed MS-Cl spectrum of the mixture.

undergoes a consecutive neutral gain/neutral loss of 44 u, and it should therefore be displayed at the NGNL spectrum, as is, indeed, observed (Figure 4b). In fact, the NGNL spectrum displays only the m/z 55 ion, also the expected result taking into account that this is the only acylium ion ($\text{CH}_2=\text{CHC}^+=\text{O}$) formed from cyclopentanone.¹¹ The consecutive NGNL MS³ scan mode can also be acquired directly, as discussed below.

Consecutive Neutral Gain/Neutral Loss MS³ Spectra. As observed in Figure 4b, a scan mode involving a sequential neutral gain and neutral loss of 44 u, applied together with the appropriate ion/molecule reaction/dissociation conditions, can serve as a very specific test for the identification of acylium ions in the gas phase. Such a scan mode was therefore directly implemented in the software used to control the pentaquadrupole mass spectrometer, which allows the simultaneous scanning of all three mass-analyzer quadrupoles with predefined mass links. Application of the NGNL scan mode to all the ions produced from ethyl vinyl ketone, 2-butanone, and acetophenone produced the MS³ spectra shown in Figure 5. As expected for ethyl vinyl ketone (Figure 5a), only the acylium ions $\text{CH}_2=\text{CHC}^+=\text{O}$ (m/z 55) and $\text{CH}_3\text{CH}_2\text{C}^+=\text{O}$ (m/z 57) respond to the consecutive 44-u NGNL test and are displayed in the spectrum. The relative abundances of these ions reflect their variable yields from the precursors, their distinct

oxirane addition reactivity,^{5e} and the different proclivities of the corresponding oxirane addition products (Scheme 1) to undergo dissociation. In the same way, only the 2-butanone acylium ions $\text{CH}_3\text{C}^+=\text{O}$ (m/z 43) and $\text{CH}_3\text{CH}_2\text{C}^+=\text{O}$ (m/z 57) appear in the spectrum shown in Figure 5b. The spectrum for acetophenone (Figure 5c) shows that, as expected, two acylium ions are produced from this precursor, that is, $\text{CH}_3\text{C}^+=\text{O}$ (m/z 43) and $\text{PhC}^+=\text{O}$ (m/z 105). It is interesting to note that an ion at m/z 77 (most likely Ph^+) also responded to the 44-u NGNL test, but an ion with such a mass cannot be ascribed to any acylium ion. Further experiments have shown that the phenyl cation (Ph^+), the most likely m/z 77 fragment of acetophenone, as well as its oxygen and sulfur derivatives, namely, the pyrilium (m/z 81) and thiapyrilium ions (m/z 97), also respond to the 44-u NGNL test and that such a scan can also be applied to their characterization.¹³

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A 3D MS² Spectrum and Its Quantitative, Qualitative, and Structural Information. The outstanding analytical utility of a MS² 3D scan, which produces an entire MS² data domain,^{2,14} is exemplified in Figure 6. This scan mode was employed to analyze, together with the membrane introduction mass spectrometry (MIMS) technique¹⁵ an aqueous solution of volatile organic compounds (VOCs), namely, 2-pentanone, toluene, and benzaldehyde. The prescan routine, as mentioned, speeds up the data acquisition, thus making this combination a very fast, sensible,¹⁵ and detailed screening for VOCs in water, as discussed in the following text.

Chemical ionization allows straightforward qualitative analysis of the mixture since only one ion, that is, the protonated molecule, is formed for each individual constituent of the mixture, which is displayed along the $m/z(Q1) = m/z(Q3)$ line (the dashed line in Figure 6a). Structure information (which would not be accessible by a simple CI experiment because no fragments of the protonated molecules are produced) can now be obtained by studying the dissociation chemistry of each constituent of the mixture. Along the horizontal Q3 axis in the 3D spectrum, or in the extracted 2D sequential product spectrum (Figure 6b–d), the fragments associated with the protonated molecules are displayed. Protonated 2-pentanone (m/z 87) fragments extensively to m/z 45, likely by loss of neutral ketene ($\text{CH}_2=\text{C}=\text{O}$); protonated toluene (m/z 93) loses almost exclusively a hydrogen molecule to yield m/z 91 (C_7H_7^+); while protonated benzaldehyde (m/z 107) loses a neutral molecule of CO to yield the abundant protonated benzene ion at m/z 79. Note the quality of structural information provided by

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these fragmentation patterns. Projection of the 3D data toward the Q1 axis (Figure 6e) allows the reconstruction of the simple MS-CI spectrum, in which the corrected abundances of each protonated molecule can then be used for quantitative analysis.

CONCLUSIONS

Multidimensional mass scans can be acquired rapidly and with high efficiency of ion transmission in pentaquadrupole instruments, provided that high-transmission quadrupoles are used and that adequate computer controlled scans are implemented, as exemplified in this study by a selective prescan procedure. A powerful set of MS³ experiments, which produce 3D and 4D mass spectra, are therefore readily available for ion chemistry studies, thus allowing convenient access to the very specific and detailed information that these spectra can provide. This considerably enhances the applicability of multidimensional pentaquadrupole mass spectrometry.

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