Reactions of Vinyl Chloride and Methanol in a Quadrupole Ion Trap Mass Spectrometer during VOC Analysis

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A reaction between vinyl chloride and the solvent (methanol) was observed during volatile organic compound (VOC) analysis on a gas chromatograph/quadrupole ion trap mass spectrometer (GC/MS). A chromatographic peak at a retention time consistent with vinyl chloride produced a mass spectrum without the characteristic chlorine isotope ions m/z 62 and 64 but instead contained an apparent molecular ion, m/z 58. The m/z 58 ion is not found in the reference spectrum of vinyl chloride. This spectrum was observed when methanol was used as solvent in internal standard, surrogate standard, or analyte solutions. Subsequent VOC standard analysis indicated that the abundance of the m/z 58 ion was directly proportional to the amount of vinyl chloride in the water samples. The correct spectrum for vinyl chloride was observed (m/z 62 and 64) when no methanol was added. From these experiments, we concluded that a reaction was occurring between the vinyl chloride and methanol in the ion trap producing a new species with a molecular ion at m/z 58. When ethanol was used as the solvent for the internal standard solution or surrogate standard, a correct spectrum of vinyl chloride was obtained.

Introduction

The flexibility (*1*) and inherent sensitivity (*2*) of the quadrupole ion trap (QIT) mass spectrometer has positioned this instrument as one of the most effective analyzers available for environmental contaminants. However, in the early years of commercial QIT, several features cast doubts on the suitability of these instruments. One of the most troubling of these features was the problem of "self-chemical ionization (self-CI)" (*3*). The self-CI problem occurred through reactions of analyte ions with neutrals present in the QIT. This self-CI problem was resolved in later versions of the instrument (*4*) and is currently not an issue regarding usage of these instruments in environmental analysis. As a result, QITs are involved in almost every aspect of environmental analysis including volatile organic compound (VOC) analysis (*5*).

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Given the above discussion, we recently switched our VOC purge/trap analyses from a Finnigan Incos 500 GC/MS (a quadrupole instrument) to a Varian Saturn 1 GC/MS (a quadrupole ion trap instrument). At this same time, a different type of VOC trap had been installed in the Tekmar Purge Trap system. While we were analyzing VOC standard solutions on the ion trap GC/MS system by using Method 524.2 (*6*), ions indicative of vinyl chloride in the standard solution disappeared. Initially, we focused on the VOC trap as a potential cause for the loss of vinyl chloride in the standard solutions. However, the VOC trap was subsequently eliminated as the cause of this problem. Closer examination of the data revealed a chromatographic peak at the retention time of vinyl chloride but with a different mass spectrum from that of vinyl chloride. The characteristic ions of vinyl chloride at m/z 62 and 64 were absent, and an ion at m/z 58 was observed (Figure 1). Since m/z 58 is not found in the reference mass spectrum of vinyl chloride, this unusual observation prompted this investigation.

Experimental Section

A Tekmar purge trap system (Tekmar Co., Cincinnati, OH) was used in this study. Helium was the purge gas with a purge pressure of 10 psi and a flow rate of 18 mL/min. Two VOC purge traps were employed, a VOCARB 4000 and a VOCARB 3000 (Supelco, Bellfontaine, PA). Spectra were acquired on a Varian Saturn 1 Quadrupole ion trap GC/MS system equipped with a RTX-Volatiles (Restec), 60 m × 0.32 mm i.d., 1.5 μm film thickness capillary GC column. Helium was used as the carrier gas for the GC/MS.

Standard purge and trap conditions were used. The sample was purged for 12 min with the VOC trap at 2 °C, then desorbed at 250 °C for 1 min. The trap was conditioned at 260 °C for 8 min at the end of each cycle.

The GC temperature program for the VOC analyses started, and the column temperature for the VOC analysis was 35 °C for 2 min, increased to 50 °C at 4 °C/min, and then increased to 210 °C at 10 °C/min and held at 210 °C for 8.25 min. All injections were made in the split mode on a Varian 1077 injector with a split flow of 20 mL/min. The injector temperature was 200 °C, and the transfer line temperature was 250 °C.

The ion trap was tuned to meet the BFB tuning requirements. The resulting segment breaks and tune factors were the following: segment 1 (time factor 120%, Rf level 32, low mass 10, high mass 70), segment 2 (time factor 70%, Rf level 32, low mass 71, high mass 78), segment 3 (time factor 100%, Rf level 32, low mass 79, high mass 150), and segment 4 (time factor 70%, Rf level 32, low mass 151, high mass 650).

Results and Discussion

The VOC trapping material was evaluated first to determine if vinyl chloride was reacting during the purge/trap cycle. No reactions were readily observed, and since the unknown (m/z 58) and vinyl chloride had identical retention times, it seemed unlikely the purge/trap unit or the gas chromatograph was the cause for the loss of vinyl chloride. Experiments using VOCARB 4000 or VOCARB 3000 VOC purge traps produced the same results, thus eliminating the VOC trap as the cause for the anomalous behavior. However, a correlation between methanol present in the spiked water samples and the magnitude of the m/z 58 peak was observed. Methanol is a commonly used solvent for spiking solutions in VOC analyses (*7*). When ethanol was substituted for methanol as
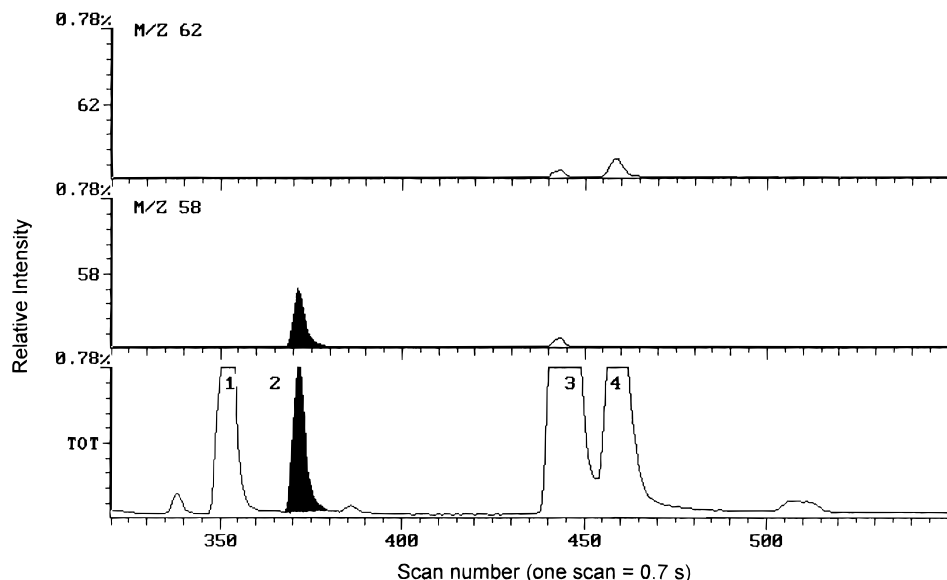
FIGURE 1. Total ion chromatogram and extracted ion chromatograms of a VOC standard (in methanol). Peaks are identified as follows: (1) chloromethane; (2) vinyl chloride; (3) bromoethane; and (4) chloroethane.
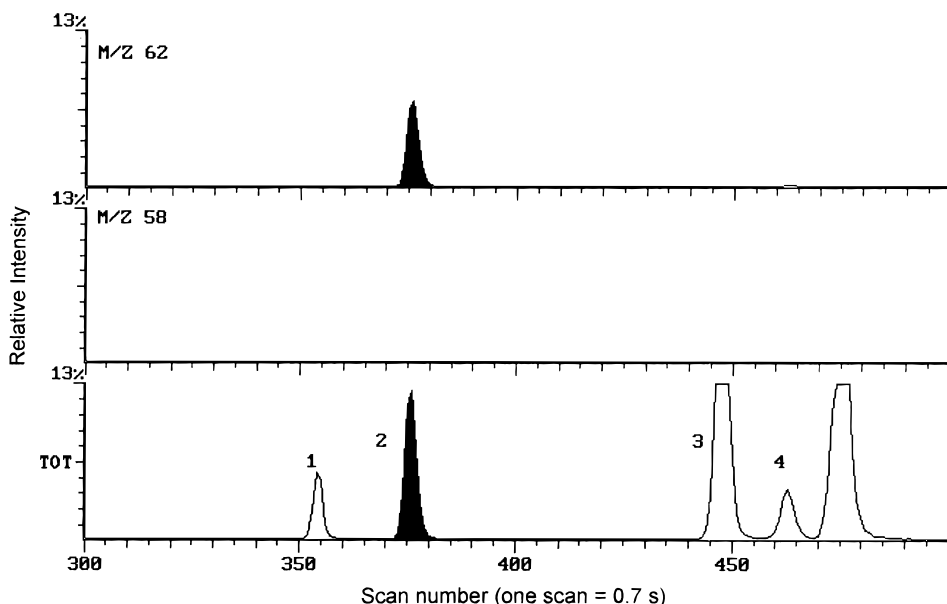

FIGURE 2. Total ion chromatogram and extracted ion chromatograms of VOC standard (in ethanol). See peak identification in Figure 1.

the solvent, a normal spectrum of vinyl chloride (m/z 62 and 64) was obtained (Figure 2), proving the involvement of methanol. Replacement of the chlorine in vinyl chloride (62 amu) with methoxy produces a compound of formula C_3H_6O (58 amu). As stated earlier, the mass spectrum of this compound does not contain ions consistent with the presence of chlorine in the molecule (8). These initial data pointed to a ion−molecule reaction between vinyl chloride and methanol analogous to the self-CI processes discussed earlier. Other groups have previously observed evidence of ion−molecule reactions involving volatile organochlorine compounds and background neutrals during VOC analysis (9, 10).

The response due to ion m/z 58, and thus the chromatographic peak intensity of the unknown, was found to be directly proportional to the concentration of vinyl chloride. In Figure 3, data for 5 VOC standard solutions, ranging in concentration from 10 to 50 ppb, are shown. The response in Figure 3 was based on the intensities of m/z 58 instead of m/z 62 from vinyl chloride. The linear regression coefficient ($r = 0.999$) indicates a high degree of correlation between

the response of the unknown compound (m/z 58) and vinyl chloride concentrations. The solvent used for the internal standard (5 μL), surrogate standard (2 μL), and analyte (0.5−2.5 μL) solutions was methanol in this set of analyses.

Another set of determinations with 8 VOC standard solutions was performed using 80 ppb of vinyl chloride but with ethanol as a solvent. Additionally, neat methanol (0−12 μL) was added to these water samples. The typical mass spectrum of vinyl chloride was observed when no methanol was added to the water sample (Figure 4a). The ion m/z 58 began to emerge in the second sample in which 1 μL of methanol was present and continued to increase with increasing methanol from 1 to 8 μL (Figure 4b). Ions from both vinyl chloride (m/z 62) and the new species (m/z 58) were observed in the same chromatographic peak when 1−8 μL of methanol was present. When methanol was increased to 10 μL or above, ions from vinyl chloride disappeared and the m/z 58 ion became the dominant feature of the mass spectrum (Figure 4c). These data indicate that vinyl chloride
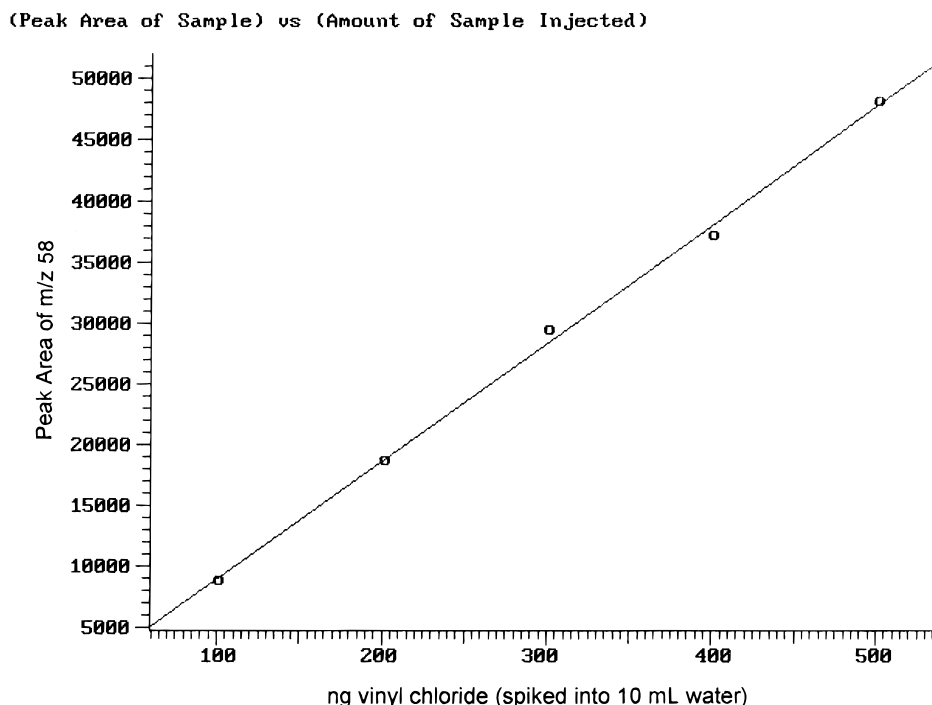
(Peak Area of Sample) vs (Amount of Sample Injected)

FIGURE 3. Calibration curve plotting the peak areas of m/z 58 verses the amount of vinyl chloride spiked into five 10 mL water samples.

was not changed when no methanol was available, but was converted into the species with m/z 58 when methanol was added. A plot of the ratio of m/z 58 to m/z 62 versus the volume of methanol added is shown in Figure 5, clearly indicating the involvement of methanol in the formation of m/z 58.

While the above discussion represents a strong case for the possibility that the species with the m/z 58 ion was the product of a bimolecular reaction between vinyl chloride and methanol in the ion trap, additional experiments were conducted to confirm this conclusion.

A vinyl chloride standard in methanol was directly injected on the column of the ion trap GC/MS. The mass spectrum produced from this experiment was identical to that produced from the VOC purge analysis. The same m/z 58 ion was found which also excluded reactions in the VOC purge and trap system.

Vinyl chloride (ethanol solvent) and methanol were analyzed separately on both the Varian ion trap GC/MS (GC Column: Rtx-Volatile, 60 m) and the Finnigan Incos 500 GC/MS (GC column: XTI-5, 30 m, cat. no. 12253). Coelution of vinyl chloride and methanol was observed on both instruments. However, in contrast to the observations on the ion trap instrument, the expected spectrum for vinyl chloride was obtained on the quadrupole system. Since coelution of the vinyl chloride and methanol was observed on both instruments, something must be unique about the operation of the ion trap that produces the species giving the m/z 58 ion. One of the major operational differences between an ion trap and a quadrupole instrument is the residence time of the ions in the instruments. In a quadrupole mass spectrometer, ions typically spend less than 10 μs in the source and in flight to the detector. However, in the QIT, the cooling period after ionization can exceed 1 ms and the overall time in the trap can exceed 100 ms, thus providing ample time for bimolecular reactions to occur. Pressure and thus mean free paths are also different for the two instruments. The source pressures in typical GC/quadrupole instruments range from 10^{-6} to 10^{-5} Torr. However, for the QIT, internal

trap pressures are 2 orders of magnitude higher (10^{-3} Torr), greatly increasing the probability of bimolecular reactions.

In an effort to further elucidate the feature responsible for the formation of m/z 58, we analyzed vinyl chloride (ethanol solvent) via the purge trap system or directly injected it into the ion trap mass spectrometer. Simultaneously, methanol was continuously introduced into the ion trap through the calibration gas inlet system that is controlled by needle valve. Since it was not possible to determine the partial pressure of the methanol in the ion trap (no vacuum gauge), the needle valve was adjusted to deliver sufficient methanol to produce an ion count similar to that obtained from the GC analysis. Mass spectra obtained from these experiments (Figure 6) were identical to those obtained when methanol and vinyl chloride were both introduced via the GC (Figure 4c), thus establishing the role of methanol in the formation of the ion m/z 58 from vinyl chloride. The ionization Rf level for the above-described experiments was m/z 32. At this Rf level, the majority of ions arising from methanol would have unstable trajectories in the trap, resulting in prompt ejection. Therefore, the observed reactions must originate from reactions of vinyl chloride molecular ions with methanol neutrals. To confirm this contention, we conducted additional experiments at increasingly higher Rf levels. At all levels, up to the ejection point of the vinyl chloride molecular ions, ions indicative of this reaction were observed (i.e., production of m/z 58). These data provide evidence for a vinyl chloride ion, methanol-neutral reaction scheme.

Several standard compounds with molecular weights of 58 (acetone, propionaldehyde, propylene oxide, allyl alcohol, and methyl vinyl ether) were analyzed in the same CI-like conditions as those in the experiment above. Ion intensities from these experiments are given in Table 1. The mass spectra of acetone, propionaldehyde, allyl alcohol, and propylene oxide are different from that of the reaction product of vinyl chloride. However, the mass spectrum of methyl vinyl ether (Figure 7) was virtually identical to the mass spectrum of the unknown reaction product. Therefore, the unknown pro-
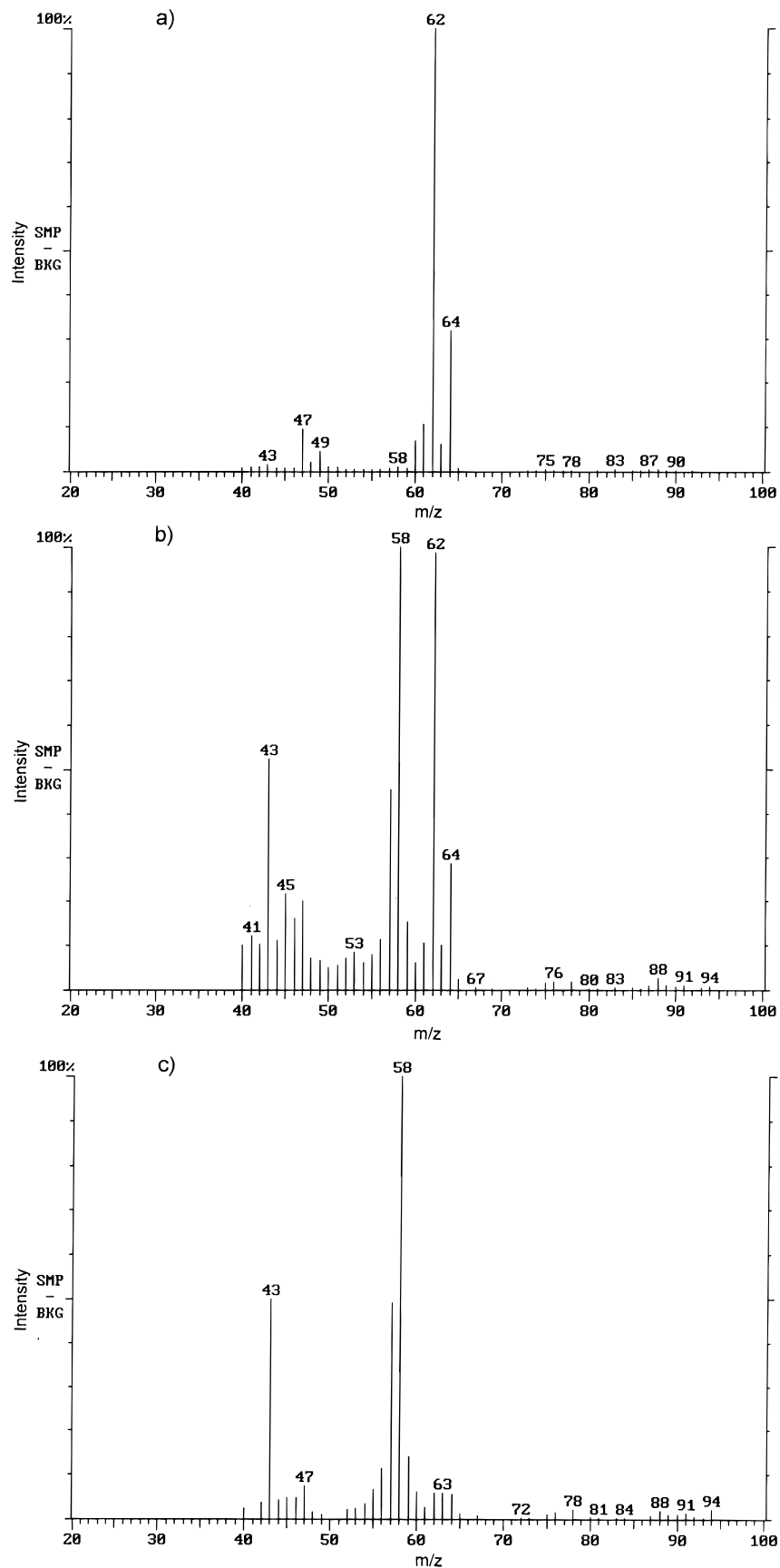
FIGURE 4. Mass spectra taken at the retention time of vinyl chloride with different volumes of methanol added: (a) no methanol added; (b) 4 μL of methanol added; and (c) 10 μL of methanol added.
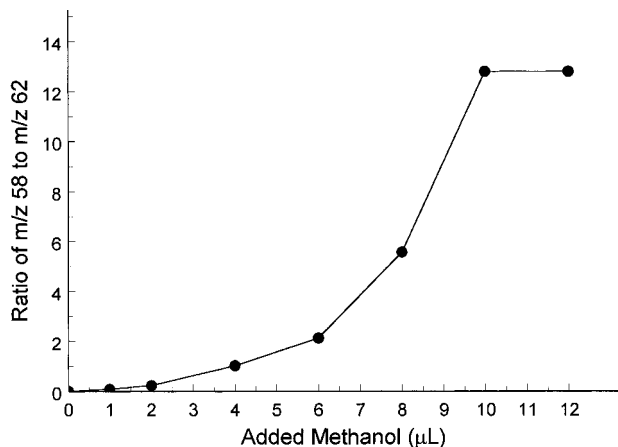
FIGURE 5. Plot of the ratios of *m/z* 58 to *m/z* 62 verses the volumes of methanol added; 800 ng of vinyl chloride was spiked into each sample.

duced from the reaction of methanol and vinyl chloride in the quadrupole ion trap was concluded to be methyl vinyl ether. We have made no effort to propose a mechanism of this reaction because the full elucidation of any gas-phase reaction mechanism would involve isotopic labeling and energy studies, which are outside the scope of this study. Johnson et al. (*10*) described the loss of ethyl chloride through reactions of water and methanol, but they provided no mechanistic details.

The ion−molecule reaction between methanol and vinyl chloride described here resulted from a relatively unique set of conditions (i.e., GC column selection, GC temperature conditions, solvent utilization, and mass analyzer). Others including the instrument manufacturer have not observed this reaction; however the mass spectrometer manufacturer used a different GC column (phase and vendor) to develop their ion trap VOC protocol.

The primary purpose of this report is to raise a precautionary note. Quadrupole ion mass spectrometry is an
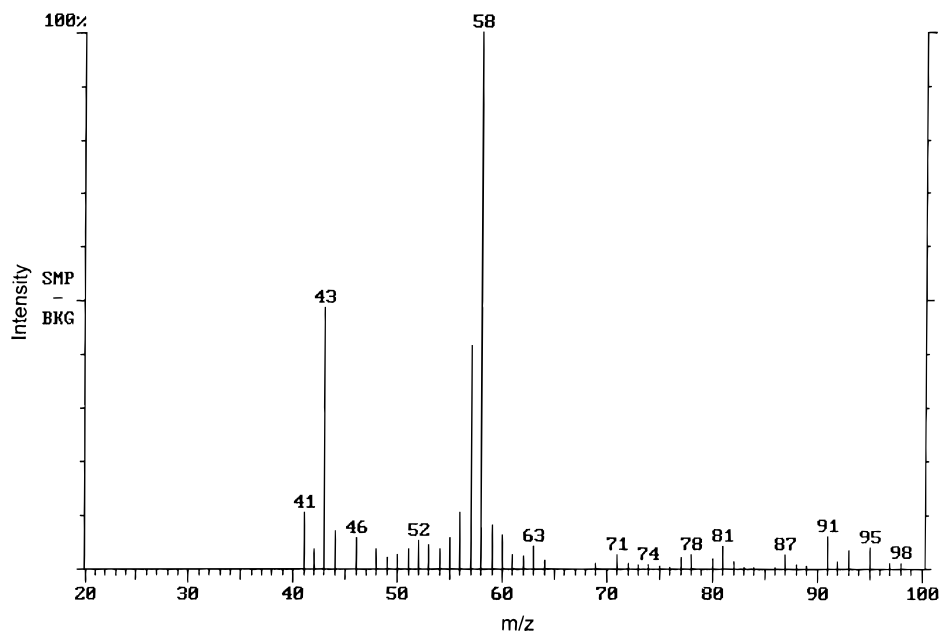

FIGURE 6. Mass spectrum obtained when vinyl chloride (ethanol solvent) was purged from a spiked water sample, chromatographically separated, and introduced into the ion trap while methanol was continuously introduced into the ion trap vacuum manifold via the calibration vial.
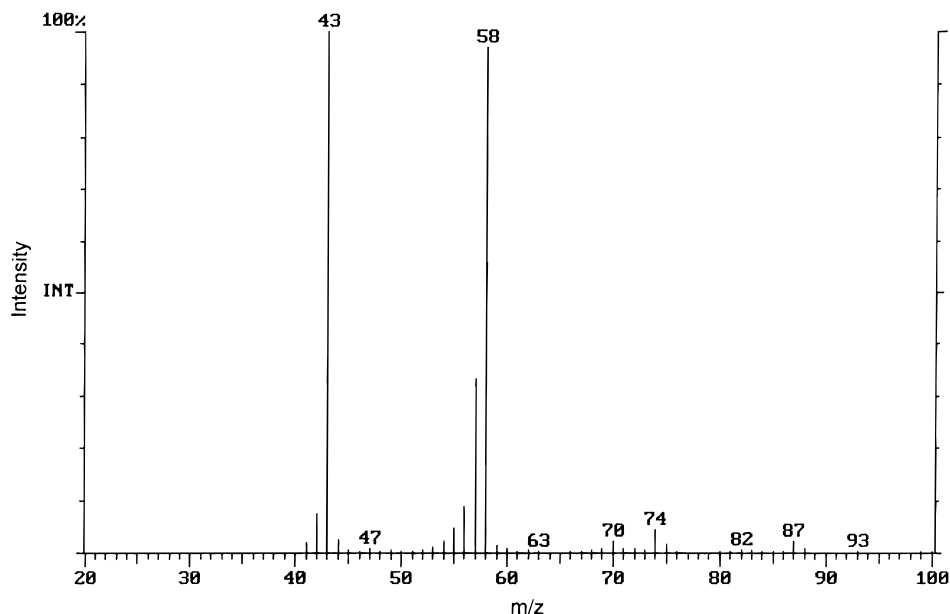

FIGURE 7. Mass spectrum of a methyl vinyl ether standard obtained under the same conditions as used in Figure 6.

TABLE 1. Relative Ion Intensities of the Major Ions from Possible Methanol/Vinyl Chloride Reaction Products (Methanol CI Data)

	m/z 43	m/z 57	m/z 58	m/z 59
propylene oxide	100	20	51	5
acetone	22	12	31	100
propionaldehyde	14	100	61	17
allyl alcohol	9	100	13	1
vinyl methyl ether	100	33	97	2
unknown	48	49	100	13

extremely valuable tool for the determination of environmental contamination. However, because of the trapping-in-time nature of the of ion trap operation, occasionally unexpected results are obtained. Care must be taken to avoid or at least minimize the occurrence of neutrals in the trap during ionization/trapping of the analyte. In this work, GC coelution of purged methanol with vinyl chloride produced conditions suitable for ion−molecule reactions. The Restec GC column that produced the coelution was a vestige of the former quadrupole analyzer-based method employed in this laboratory. The reactions of vinyl chloride and methanol can be avoided if methanol is not employed as the VOC solvent. This potential solution presents certain method conflicts. A much better solution would be to avoid coelution of vinyl chloride and methanol through manipulation of GC retention times (column-phase selection and temperatures). The latter choice was our solution to the problem.

Literature Cited

(1) March, R. E. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 1543.

(2) Cairns, T.; Chiu, K. S.; Navarro, D.; Siegmund, E. G. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 1976.

(3) McLuckey, S. A.; Glish, G. L.; Asano, K. G.; Van Berkel, G. J. *Anal. Chem.* **1988**, *60*, 2312.

(4) Yates, N. A.; Booth, M. M.; Stephenson, J. L., Jr.; Yost, R. A. In *Practical Aspects of Ion Trap Mass Spectrometry*; March, R. E., Todd, J. F. J., Eds.; CRC Press: Boca Raton, FL, 1995; Vol. 3, p 121.

(5) Budde, W. L. In *Practical Aspects of Ion Trap Mass Spectrometry*; March, R. E., Todd, J. F. J., Eds.; CRC Press: Boca Raton, FL, 1995; Vol. 3, p 438.

(6) EPA Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*; U. S. Environmental Protection Agency, EPA-600/R-95/131, August, 1995.

(7) (a) Janicki, W.; Wolska, L.; Wardencki, W.; Namiesnik, J. *J. Chromatgr. A* **1993**, *654*, 279. (b) Buszka, P. M.; Rose, D. L.; Ozuna, G. B.; Groschen, G. E. *Anal. Chem.* **1995**, *67*, 3659. (c) Lee, M. R.; Lee, J. S.; Hsiang, W. S.; Chen, C. M. *J. Chromatgr. A* **1997**, *775*, 267.

(8) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed., University Science Books: Mill Valley, CA, 1980; pp 16−18.

(9) Bauer, S.; Solyom, D. *Anal. Chem.* **1994**, *66*, 4422.

(10) Johnson, E.; Louris, J.; Tucker, D.; Bradshaw, S.; Booth, M.; Hartford, R.; Stafford, G. *Proc. 39th ASMS Conference on Mass Spectrometry and Allied Topics*; Nashville, TN, 1991; p 1289.