ION MOBILITY SPECTROMETRY AS A FIELD SCREENING TECHNIQUE

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1. INTRODUCTION

Ion Mobility Spectrometry (IMS), also called Plasma Chromatography, is used to detect trace quantities of organic vapors in gaseous mixtures. Several researchers over the past 15 years have demonstrated the utility of mobility detection for a variety of organic compounds.[1-11] Quantities as low as 10^{-10} grams of nitrosamines have been reported[12].

IMS is a conceptually simple technique that relies on the drift time, or time of flight, of molecular, or cluster, ions through a host gas as a means of differentiation. This differs from classical mass spectrometry in that there is little, if any, fragmentation and the ions are not mass analyzed. Detailed theory can be found elsewhere.[13-15] The ions are differentiated by charge and by mobility. The reduced mobility K_0 (corrected for standard pressure and temperature) is expressed as

$$K_0 = 42.51\ D$$

where D is the scaler diffusion coefficient of Fick's law. This reduced mobility K_0 is catalogued and identified for each ionic species present.

2. EXPERIMENTAL

The work was performed on a MMS-290 Ion Mobility Mass Spectrometer (PCP, Inc.). shown in figure 1 and an Air Vapor Monitor made by Graseby Ltd.

The PCP, Inc. MMS-290 spectrometer used in these experiments consists of an ion mobility spectrometer followed by a quadrapole mass spectrometer coupled to a Nicolet signal averager with a computer interface for storage, data manipulation and display.

There are four modes of operation for the MMS-290. In the total ion mode the MMS-290 acts as an ion mobility spectrometer. Ions are gated into the drift region and detected by the electrometer. All ions detected are averaged, stored and displayed. In the integral ion mode the mass spectrometer is the detector instead of the electrometer. Again, all ions are detected, averaged, stored and displayed. There is no mass analysis in this mode. It is used to check that the ion distribution is not changed by traveling the extra distance through the mass spectrometer. The third mode is the mass spectrum. The shutter grid is held open to allow a continuous stream of ions into the mass spectrometer which is mass analyzing the ions. This provides a mass spectral scan of the total ion flux. The last mode of operation is the tuned ion mode where the MMS-290 is operated as in the integral ion mode but the mass spectrometer is only detecting one mass ion at a time. This shows which mass ions are associated with each mobility peak.

The Airborne Vapor Monitor (AVM) used in these experiments consists of an IMS described above with a membrane inlet and internal electronics for signal processing and alarm. It operates in both positive and negative ion mode, has

no internal display but can be interfaced to a personal computer for display and storage of the IMS spectra. The AVM has only an electrometer, it has no mass spectrometer to mass analyze the ions, and it operates as the total ion mode of the MMS-290.

Air, or the sample gas, is drawn into the ionizing region and is ionized by 60 keV Beta rays from a radioactive Ni63 source. A potential exists between the ionizer and the collector forcing the ions in the direction of the shutter grid. The closed shutter grid neutralizes all ions reaching it. The shutter is pulsed open for approximately 0.1 millisecond (msec) and a cross section of the ions flow into the drift region. The shutter closes again isolating a short pulse of ions that travel down the drift region propelled against the drift gas flow by the potential on the collector. The ions are differentiated by their charge in the electric field and their mobility in the drift gas (velocity V_d)

$$V_d = K E.$$

The IMS differentiates the ions because by the time that they reach the shutter grid the ion molecule reactions have equilibrated and in the drift region no more reactions take place.

As the separated ions reach the collector, they are detected by a fast electrometer, and a current is generated directly proportional to the number of ions. The resultant spectrum is depicted in figure 2 [16].

The highest K_0 ions (C+) are usually smaller or more compact followed by the slower ions B+ and A+, in time.

Both positive and negative ion formation of reactant and product ions are multistep processes. Good, Durden, and Keburle[17] have determined the mechanisms involved in positive reactant ion formation:

$$N_2 \xrightarrow{\beta^-} N_2^+ + e^-$$

$$N_2^+ + 2\,N_2 \longrightarrow N_4^+ + N_2$$

$$N_4^+ + H_2O \longrightarrow H_2O^+ + 2\,N_2$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$H_3O^+ + H_2O + \cdot N_2 \longrightarrow (H_2O)_2H^+ + N_2$$

The size of the resultant reactant ion water clusters depend upon the relative humidity but generally water chemistry dominates the positive ion mode. The water ion may cluster directly with the sample molecule M or, as is the case more often, the sample molecule abstracts the proton from the water cluster and then may attract more or less water molecules depending on the humidity. At high concentrations the sample molecules may form dimers with a proton. Whenever there is some other molecules present with a higher proton affinity than water they may replace the water in the above mechanisms i.e. Acetone or NH_3. So, in figure two peak C may be the reactant ion, B the hydrated monomer, and A the protonated dimer.

Negative reactant ion formation as summarized by Spangler and Collins[18] include the following:

$$e^-(\text{thermal}) + O_2 \longrightarrow O_2^-$$

$$O_2^- + CO_2 \longrightarrow CO_2\,O_2^-$$

$$O_2^- + nH_2O \longrightarrow (H_2O)_n\,O_2^-$$

where n = 1,2.

The sample molecule can cluster with the O_2^- or abstract the O_2^- from the CO_2. As can be easily seen, the chemistry can be quite involved before any products are formed.

The operating parameters for the MMS-290 were;

Cell length	15 cm
Operating voltage	3000 volts
Electric field	200 volts/cm
Carrier gas	200 ml/min
Drift gas	500 ml/min
Cell Temperature	40 °C
Pressure	Entered Daily
Drift distance	10 cm

The AVM was operated as received from Graseby Analytical, Ltd.(Watford, Herts, UK). Signals from this IMS were processed with a Graseby Analytical, Ltd., advanced signal averaging (ASP) board installed in an IBM PC/AT computer. Known or approximate operating conditions were;

inlet flow	500 ml/min.
Drift tube temperature	ambient
membrane temperature	70 °C
reaction region	2.2 cm
drift region	~3.8 cm
field gradient	~ 200 V/cm

The samples were generated using a Q-5 apparatus, (where a saturated vapor stream is mixed with a high volume diluent dry air stream). By varying the quantities of both streams the concentration of sample in the diluted vapor stream was controlled. The resulting diluted vapor stream was sampled by either the IMS/MS inlet or the AVM. All samples were used as received from the manufacturer. The concentration of the saturated vapor stream was calculated from vapor pressure data or from the Antoine equation.

3. RESULTS AND DISCUSSION

The data following are an example of the power of this detection system to high concentration vapors of acetic acid. The acetic acid was used "as is", and, as will be shown, was contaminated with acetic anhydride(as is often the case). The target concentration for acetic acid

detection with the AVM was the Time Weighted Average (TWA) of 10 ppm[19], the Short Term Exposure Limit (STEL) of 15 ppm[19], up to the Immediately Dangerous to Life or Health (IDLH) level of 1000 ppm[20]. Figures 3-6 show the response of the AVM for these three concentrations.

The identity of the peaks in the above data was determined with the IMS/MS in the following manner. First, the reduced mobility is calculated for each peak. Since the reduced mobility is a factor of pressure and temperature and these vary in the AVM and between the AVM and IMS/MS, a drift time ratio is calculated by dividing the specie mobility by the reactant ion mobility (both are under the same temperature and pressure). Then, the IMS/MS is operated in the total ion mode and the integral ion mode to check that there is no effect between the different inlets of the AVM and the IMS/MS and that the mass spectrometer entrance of the IMS/MS does not change the specie (figures 7 and 8). The first thing noticed is that the pinhole inlet of the IMS/MS is much more sensitive than the membrane of the AVM. The membrane is required, however, to keep too much water and contaminants from spoiling the sensitive IMS cell. So, allowing for the difference in sensitivity, the mobility spectrum of the IMS/MS is compared with the AVM to correlate the mobility peaks between the two instruments. Once confirmed, the mass spectrum is taken to determine what mass species are the major contributors to the ion mobility spectrum (figure 9). Then, each mass is scanned in the tuned ion mode to determine to what peak in the mobility spectrum each mass contributes (figure 10). As can be seen, in this low concentration, the masses 55,73,83,101,and 129 are all hydrates and "nydrates" of the H^+ "reactant ion" and the masses 79, 97, 125, and 153 are hydrates and "nydrates" of the H^+ acetic acid monomer. The concentration is then increased and the analysis series is repeated. As the concentration increases the mass spectrum becomes more complicated but assignments can be made bases upon past experience. Since, at this time, we do not have the capability there is no secondary mass fragmentation for confirmation of these species. Tables 1 indicates the assignments for each mass fragment in the mass spectrum. Table 2 is a list of the mobility ratios and the assignments for each mobility peak seen at the various concentrations.

CONCLUSION

This example of acetic acid illustrates the potential of this hand held ion mobility spectrometer to differentiate between regulated concentrations of hazardous chemicals. In support of another program this work has been extended to identification of these regulated concentrations (TWA, STEL, and IDLH) of 15 other solvent chemicals. Although limited in scope, by extending this data base the AVM could be used as a field screening device and as a safety device for field personnel.

TABLE 1

AMU	Specie	Comment
55	$H^+(H_2O)_3$	reactant ion
73	$H^+(H_2O)_4$	reactant ion
79	m $H^+(H_2O)$	monomer hydrate
83	$H^+(H_2O)_3+N_2$	reactant ion
97	m $H^+(H_2O)_2$	monomer hydrate
101	$H^+(H_2O)_4+N_2$	reactant ion
125	m $H^+(H_2O)_2+N_2$	monomer "nydrate"
129	$H^+(H_2O)_4+2N_2$	reactant ion
153	m $H^+(H_2O)_2+2N_2$	monomer "nydrate"

TABLE 2

Mobility Ratio	Assignment	
1.00	$H^+(H_2O)_x(N_2)_y$	Reactant Ion
1.08-1.09	m $H^+(H_2O)_x(N_2)_y$	Acid Monomer
1.18-1.24	m_2 $H^+(H_2O)_x(N_2)_y$	Acid Dimer
1.34-1.35	m n $H^+(H_2O)_x(N_2)_y$	Acid Anhydride
1.47-1.48	n_2 $H^+(H_2O)_x(N_2)_y$	Anhydride Dimer

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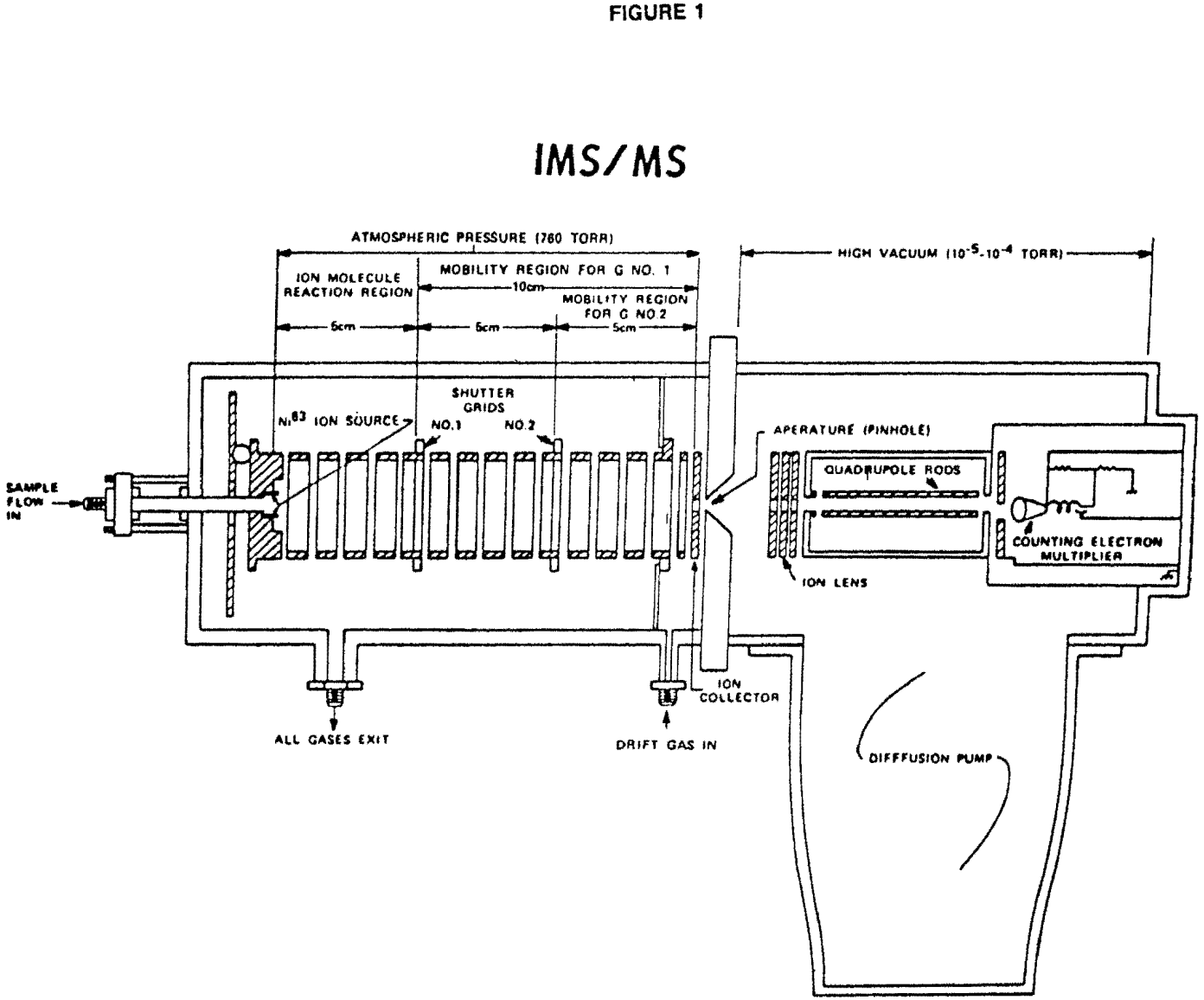
FIGURE 1


IMS/MS
ATMOSPHERIC PRESSURE (760 TORR)
HIGH VACUUM (10^{-5}-10^{-4} TORR)
ION MOLECULE REACTION REGION
MOBILITY REGION FOR G NO. 1
10cm
MOBILITY REGION FOR G NO.2
5cm
5cm
5cm
SHUTTER GRIDS
Ni^{63} ION SOURCE
NO.1
NO.2
APERATURE (PINHOLE)
QUADRUPOLE RODS
COUNTING ELECTRON MULTIPLIER
SAMPLE FLOW IN
ION LENS
ION COLLECTOR
ALL GASES EXIT
DRIFT GAS IN
DIFFFUSION PUMP

TYPICAL [ION ARRIVAL TIME SPECTRUM]

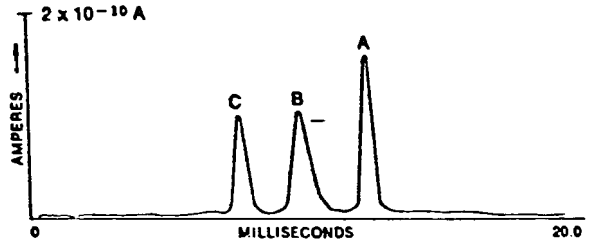


FIGURE 2

Figure 3: AVM Spectrum (Air)

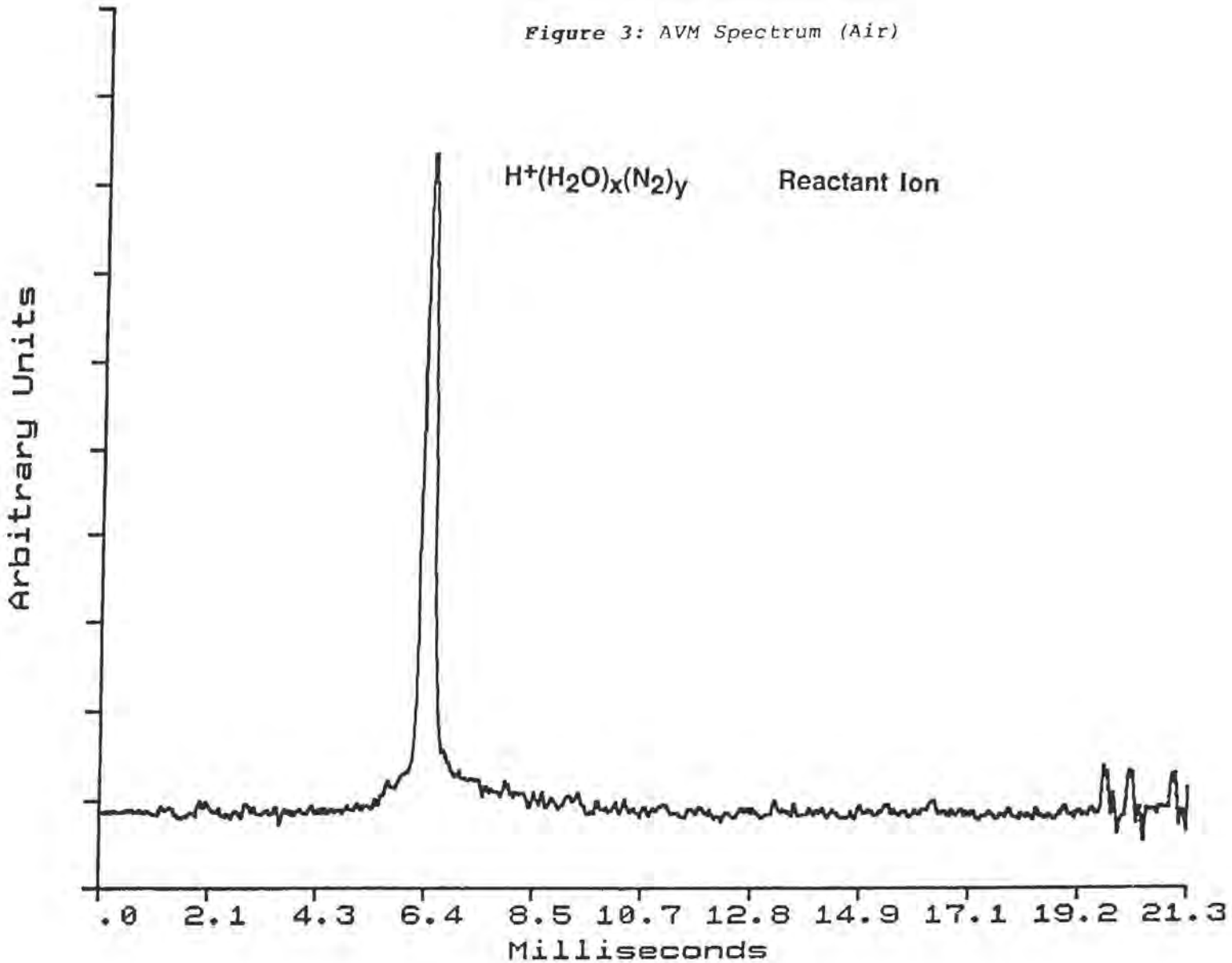


Figure 4: AVM Spectrum (Acetic Acid 10 ppm)

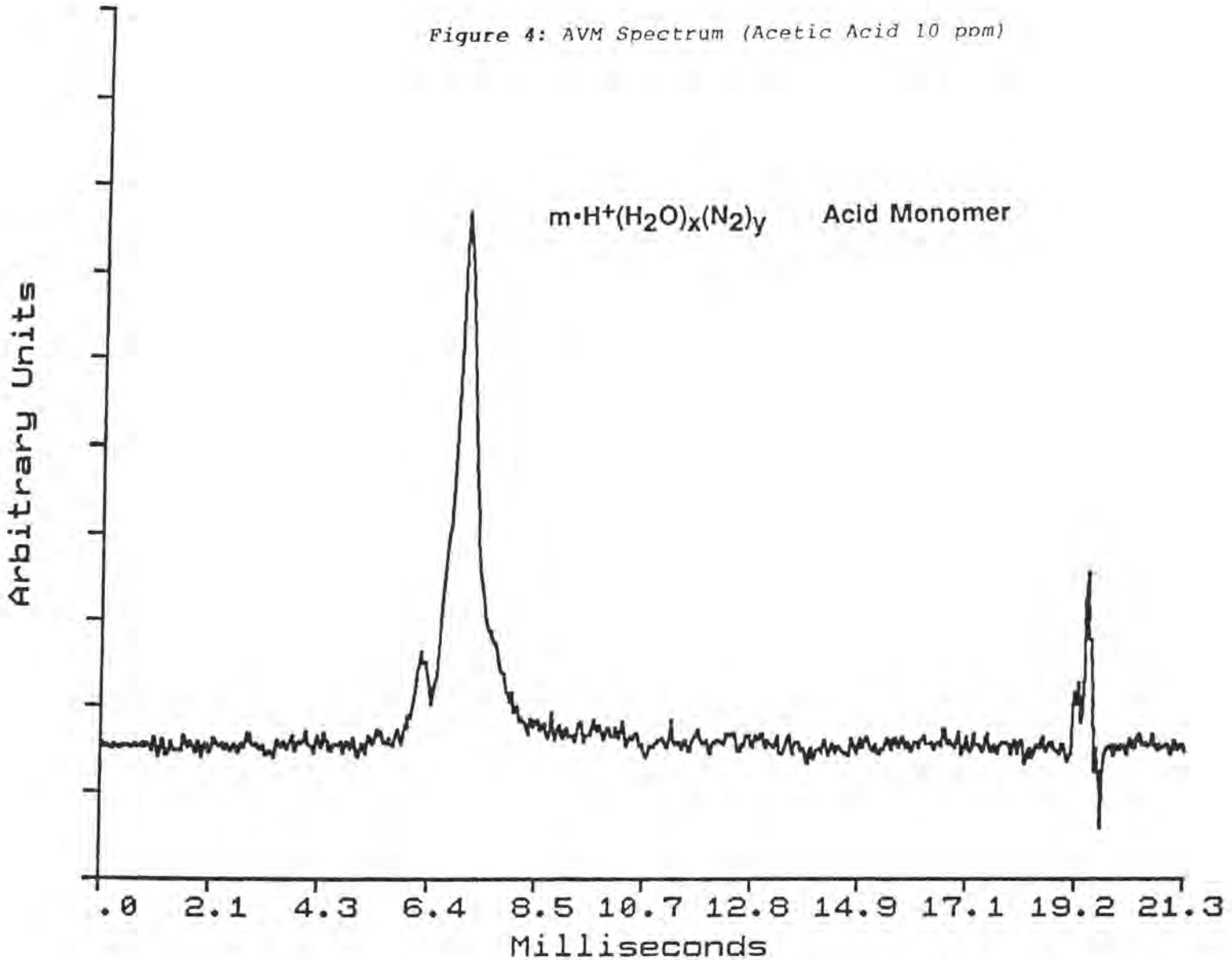


Figure 5:AVM Spectrum (Acetic Acid 15 ppm)

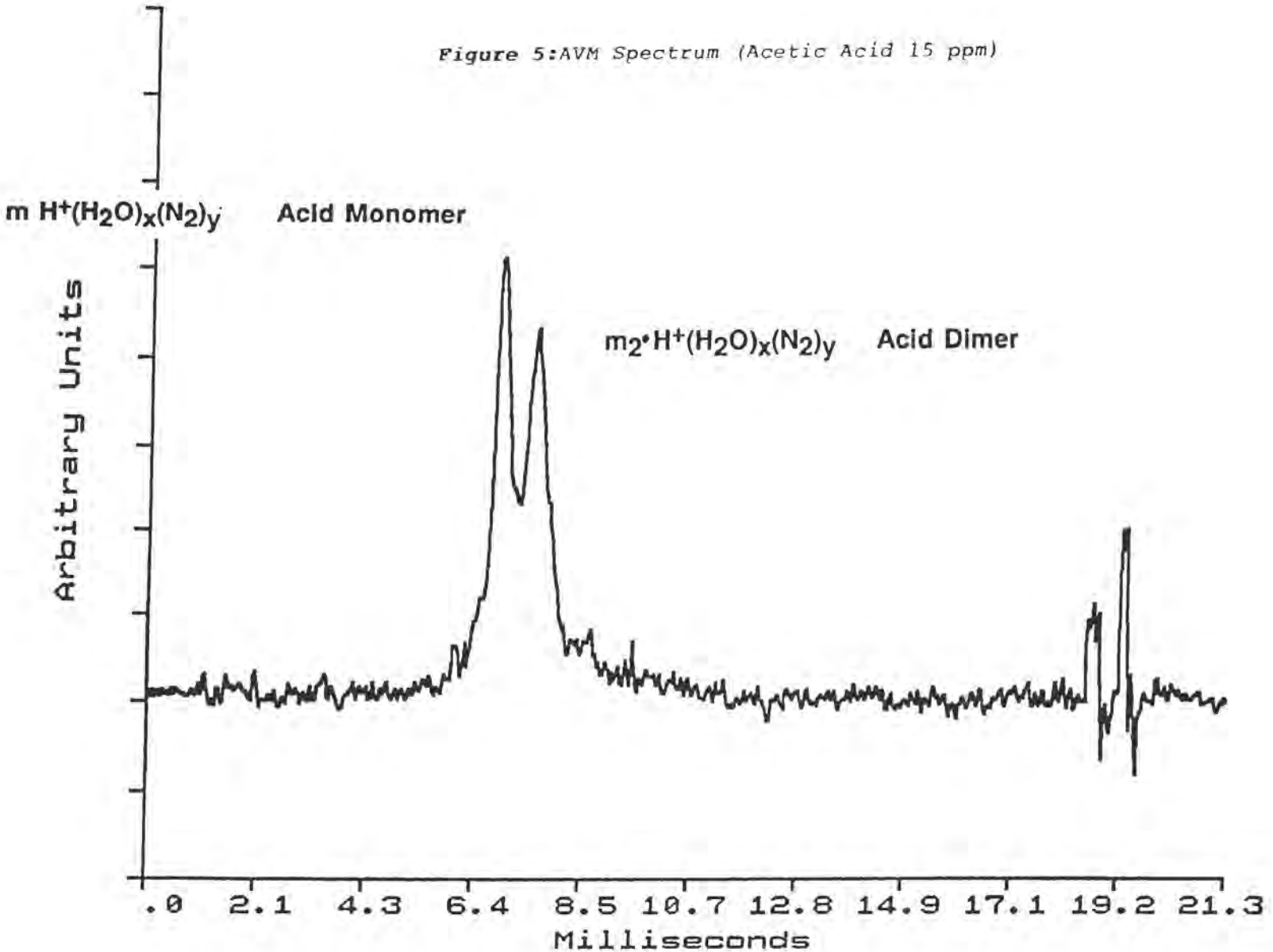
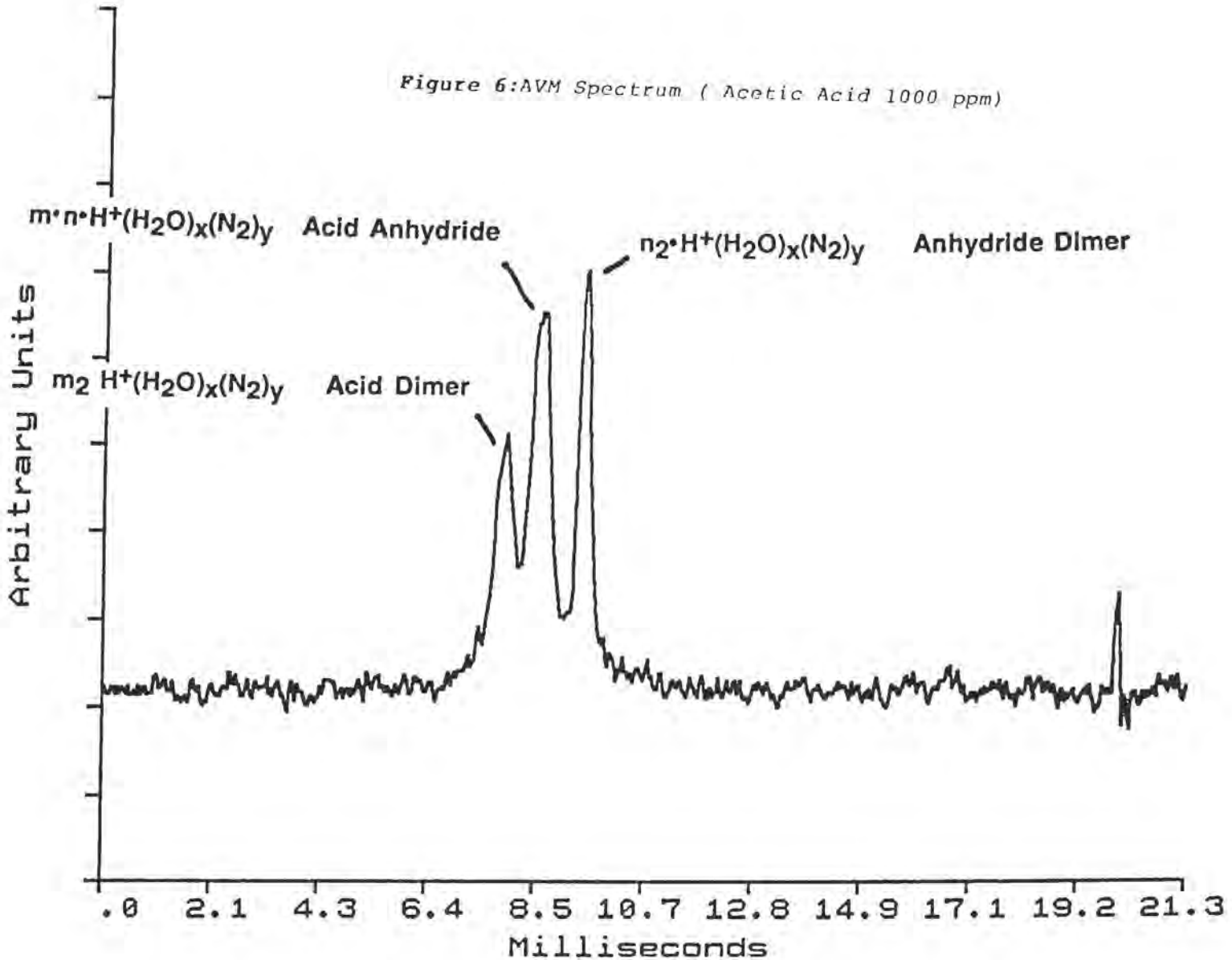


Figure 6:AVM Spectrum (Acetic Acid 1000 ppm)



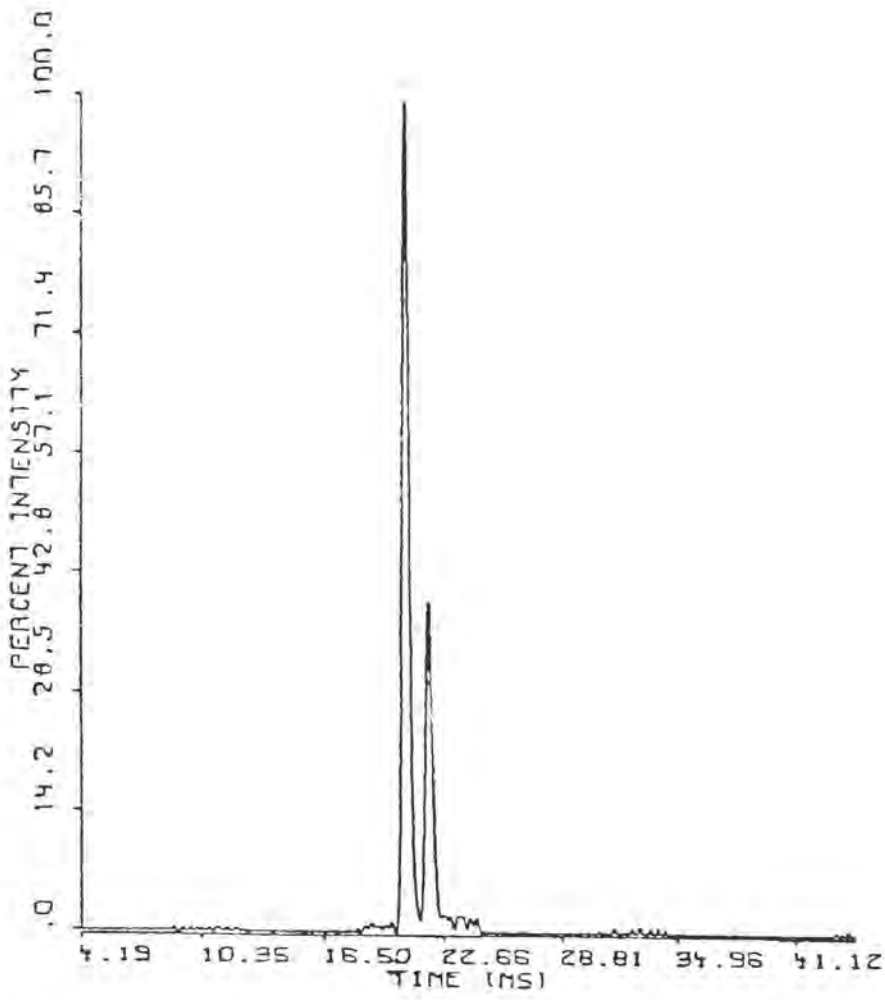


Figure 7: *IMS/MS Spectrum "Total Ion Mode" (Acetic Acid 80 ppb)*

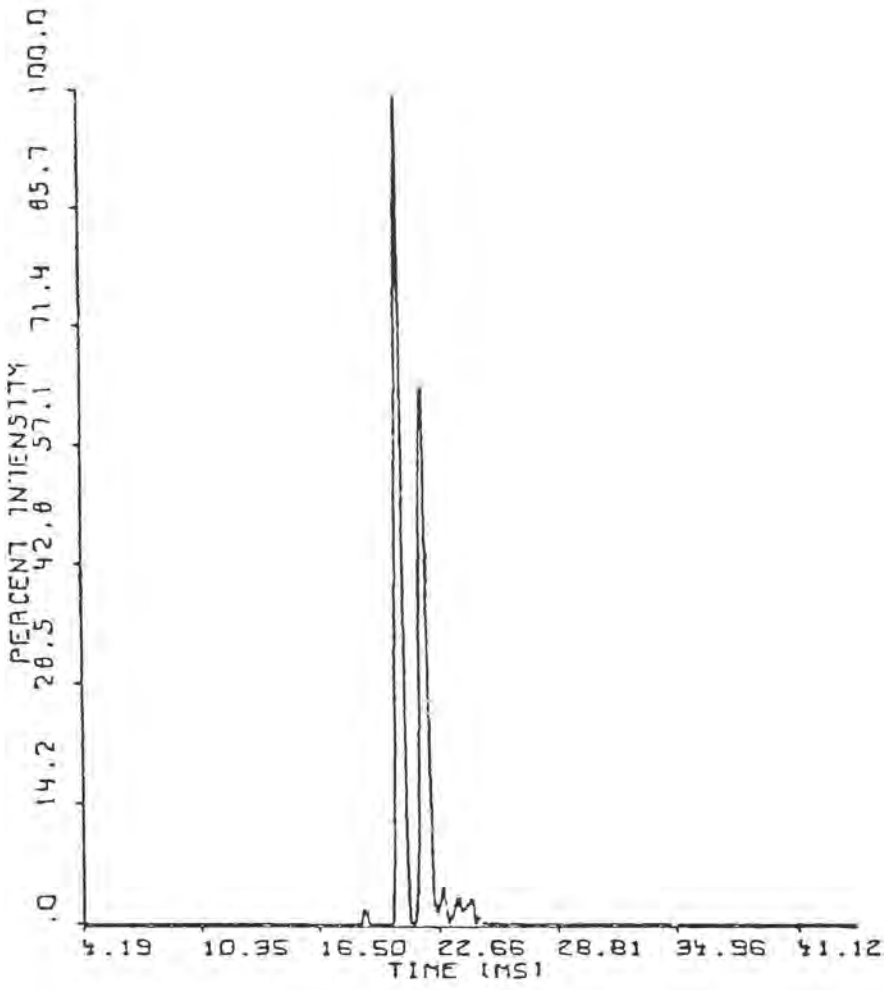


Figure 8: *IMS/MS Spectrum "Integral Ion Mode" (Acetic Acid 80 ppb)*

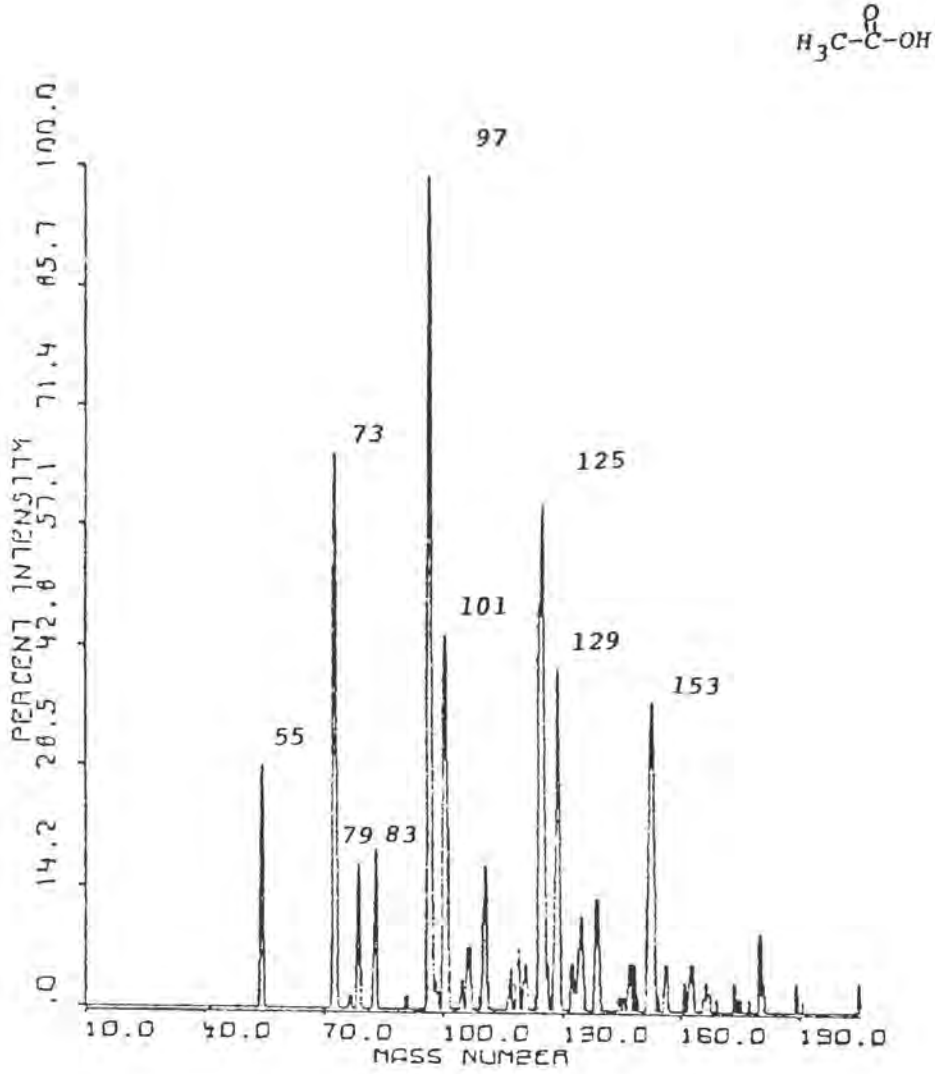


Figure 9: *IMS/MS Spectrum "mass spectrum mode" (Acetic Acid 80 ppb)*

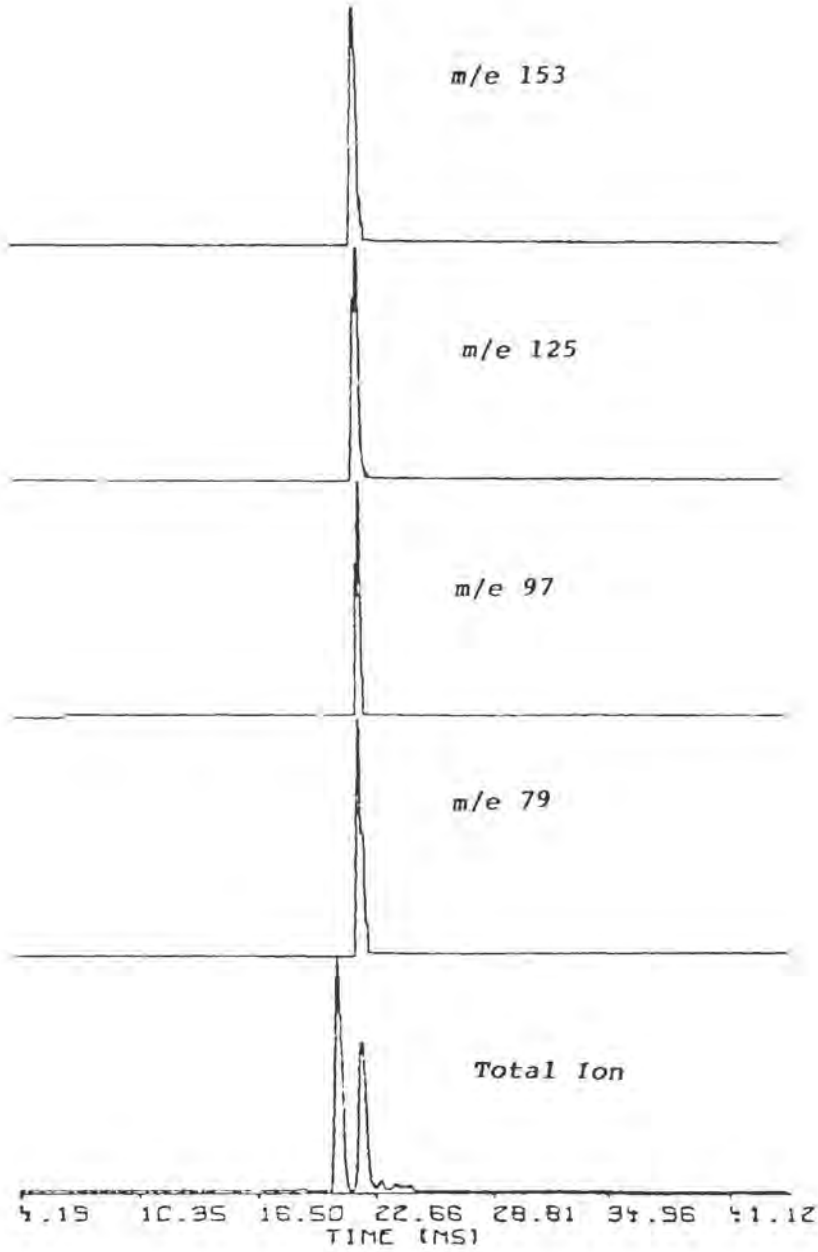


Figure 10: *IMS/MS Spectra "Tuned Ion Mode" (Acetic Acid 80 ppb)*

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