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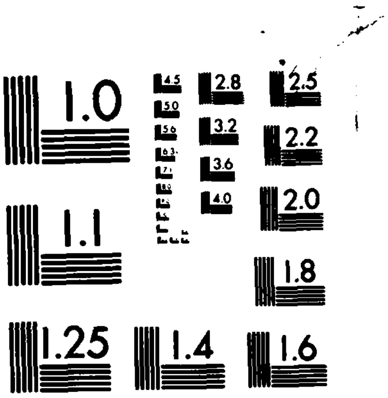

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TECHNICAL REPORT
ARCSL-TR-83056

MOBILITY AND MOLECULAR IONS OF DIMETHYL METHYL PHOSPHONATE, METHYL SALICYLATE, AND ACETONE

By

Daniel M. Nowak

June 1983

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The mobilities of positive and negative reactant ions are reported for $(H_2O)_nH^{(+)}$; $(H_2O)_2O_2$ and $(H_2O)_2CO_3^{(-)}$ ion clusters. The formation of positive DMMP monomer and dimer is reported, and equilbria molecular reactions are reported. Acetone is reported as forming a dimer at 81 ppb with a reduced mobility (K_0) of 1.82. Methyl salicylate is shown to form a protonated and hydrated positive monomer. Mixtures of DMMP and methyl salicylate with acetone

20. ABSTRACT (continued)

showed a substantial change in DMMP ion clustering and little or no change in the methyl salicylate mobility spectra. Negative ions were not observed for DMMP, methyl salicylate, acetone and the mixtures under the conditions reported.

PREFACE

The work described in this report was authorized under project 1L162706A553-H. This report was started in January 1983 and completed in May 1983.

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MOBILITY AND MOLECULAR IONS OF DIMETHYL METHYL PHOSPHONATE, METHYL SALICYLATE, AND ACETONE

1. INTRODUCTION

Ion Mobility Spectrometry (IMS), also called Plasma Chromatography, is an analytical technique used to detect, identify, and quantify trace quantities of organic vapors in gaseous mixtures. IMS is recognized as a simple technique for identification of specific organic molecules without using cumbersome, expensive mass spectrometers. Previous work has shown excellent detection sensitivity for trace quantities of pesticides,[1] TNT,[2] nickel carbonyl,[3] and phosphorus esters.[4] Extensive work by several researchers over the past decade has demonstrated the utility of mobility detection for a variety of organic compounds.[5,6] Detection of 10^{-10} grams of nitrosamines has been reported.[7] Positive reactant ion studies were reported by Karasek, et al,[8] and mass identified mobility spectra of $(H_2O)H^+$, NO^+, $(H_2O)_2H^+$ and $(H_2O)N_2H^+$ were reported. Negative reactant ions were reported by Spangler and Collins[9] and O_2^-, $(H_2O)_2^-$, and CO_4^- are proposed.

A detailed review of IMS theory, applications, and chemistry will not be made here; but texts by McDaniel and Mason,[10] Bowes,[11] and Ausloos[12] provide excellent background information. Several reviews[13,14,15,16,17] provide summary information on IMS technology and instrumentation.

The current work used an MMS-290 Ion Mobility Mass Spectrometer to determine mobilities of dimethyl methyl phosphonate (DMMP), methyl salicylate, and acetone. Mixtures of acetone/DMMP and acetone/methyl salicylate were studied and the effect on molecular ion formation and mobilities are reported. Both positive and negative mobilities are reported for each compound and mixtures with acetone. The molecular ions contributing to each mobility were mass identified using a quadrapole mass spectrometer

2. THEORY

Ion Mobility Spectrometry is based on the drift, or time of flight, of molecular ions in a host gas in the presence of a uniform electric field. The physical basis for IMS is the diffusion and mobility of gases.

The diffusion of gases is defined by Fick's law

$$J = -D\nabla n, \qquad \text{(Equation 1)}$$

where n is the number density of ions; D is the scalar diffusion coefficient; and J is the ionic flux density.

Molecular ions in a uniform gas at constant temperature and pressure will diffuse uniformly in all directions in the host gas if the ion density is small enough to ignore coulombic forces. The flow of ions under these conditions is from the higher concentration of ions to a lower concentration (negative in equation 1). The ionic flux density (J) is the ease with which ions flow, or diffuse, in the host gas and is the number of ions flowing through a cross-sectional area normal to the direction of flow per unit time. Therefore, D is a joint property of the ions and the host gas. The velocity, V, of the diffusing ions is

$$J = nV \quad . \qquad \text{(Equation 2)}$$

Therefore, Fick's law is rewritten as

$$V = \frac{-D\nabla n}{n} \quad . \qquad \text{(Equation 3)}$$

Now consider the same conditions of temperature, pressure, ion density, and host gas with a weak electric field applied to the gas mixture. The electric field induces electromagnetic lines of force on the ions. The drift velocity, V_d, of the ions is now greater than the diffusion velocity and is proportional to the electric field, E.

$$V_d \propto E \qquad \text{(Equation 4)}$$

The drift velocity becomes

$$V_d = KE \quad , \qquad \text{(Equation 5)}$$

when the constant of proportionality, K, for the mobility of ions is applied. The drift velocity is the distance, d, the ions travel per unit time, t. Substituting and rearranging equation 5, the mobility is

$$K = \frac{d}{tE} \quad . \qquad \text{(Equation 6)}$$

Both mobility and diffusion are a joint property of the ions and the host gas. The relationship of diffusion and mobility was first recognized by Nernst in 1888 and later by Townsend and Einstein and is expressed as

$$K = \frac{eD}{kT} \quad , \qquad \text{(Equation 7)}$$

where e is the ionic charge (1.6021×10^{-19} coulombs); k is Boltzman's constant (1.3806×10^{-23} joule/°K); and T is temperature (°K).

If K is expressed in units of cm^2/volt sec, D as cm^2/sec and e and k are substituted, equation 7 becomes

$$K = 1.1605 \times 10^4 \frac{D}{t} \quad . \qquad \text{(Equation 8)}$$

Mobility is usually expressed as reduced mobility at standard temperature and pressure. Therefore, the reduced mobility, K_0, for equation 6 becomes

$$K_0 = \frac{P}{760} \frac{273}{T} K = \frac{P}{760} \frac{273}{T} \frac{d}{tE} \quad , \qquad \text{(Equation 9)}$$

and equation 8 becomes

$$K_0 = \frac{1.1605 \times 10^4 D}{273°K} = 42.51 D \quad . \qquad \text{(Equation 10)}$$

3. MOBILITY SPECTROMETRY

The theory of ion mobility has resulted in many designs of drift tubes for generating ions and measuring the time of flight. Despite these various designs, experimental data are correlatable when reduced mobilities are calculated and mass spectrometer identification of ions is used. The ion mobility spectrometer used in this experiment is schematically shown in figure 1 and is part of the MMS-290 system.

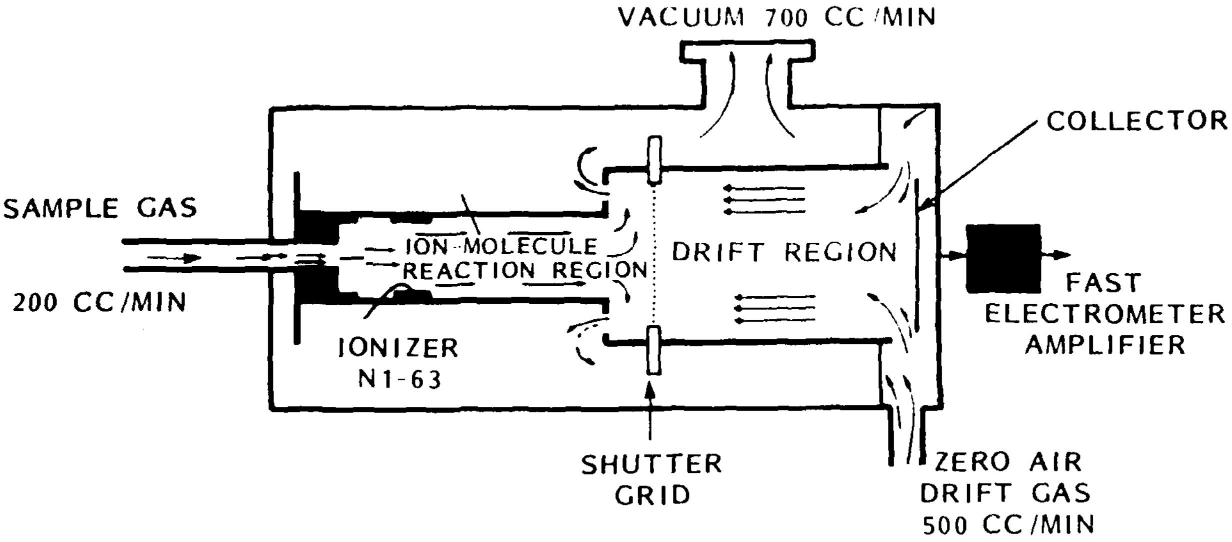


Figure 1. Ion Mobility Spectrometer

Air, or the sample gas, is drawn into the ionizer region and is ionized by 60 kev Beta rays from a radioactive Ni63 source. The ionized molecules flow through the reaction region under the influence of an electric field generated by rings surrounding both the reaction and drift regions. As the ions reach the closed shutter grid they are neutralized. If negative ions are under study, the shutter grid has a positive potential. A negative shutter grid potential is used for positive ion studies. The shutter grid is pulsed open for approximately 0.1 millisecond and a cross section of the air and ions flow into the drift region. The grid again closes cutting off additional flow of ions into the drift region. The pulse of ions drift down the drift region under the influence of the electric field and separate into distinct packages or a front of ions. This separation is due to the different velocities and is defined by equation 5.

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 time of flight of the separated ions from the shutter grid to the collector, the fixed distance of travel, and the applied electric field are the parameters used to calculate ion mobilities using equation 9. A stylized mobility (drift) spectrum is shown in figure 2. The processes of ionization, reaction, extraction, and separation are shown in figure 3. The arrival time spectrum shows that the smaller ions (A^+) arrive at the collector faster than the heavier

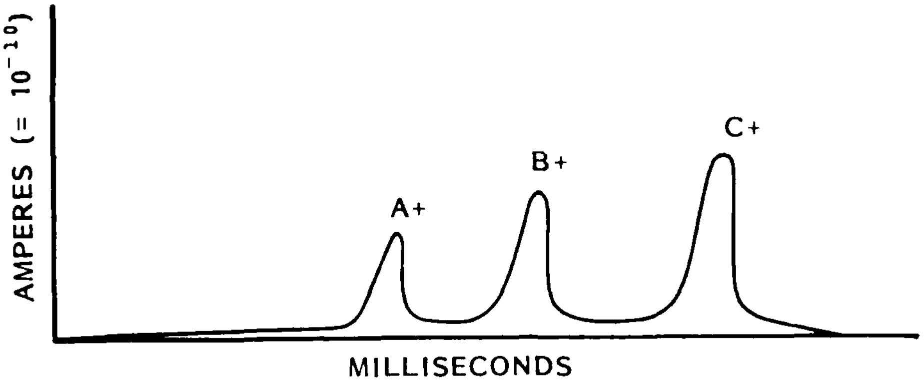


Figure 2. Mobility (Drift Time) Spectrum

(C^+ and B^+) ions. The smaller ions have the higher mobilities. The drift time of the sample ions is dependent upon the size and shape of the ions, if all other variables are constant. Therefore, the drift time is a measure of ion mass, since ion molecule size is generally related.

4. REACTANT AND PRODUCT ION MECHANISMS

Positive and negative ion formation in IMS is a multistep process involving ionization, ion formation of reactant ions through charge (or proton) transfer, attachment, abstraction, and cluster reactions.

The mechanism for positive ion formation of reactant and product ions have been reported by Good, Durden, and Keburle[18] and involve the following reactions:

$$N_2 \xrightarrow{\beta^-} N_2^+ + e^- \qquad \text{(Equation 11)}$$

$$N_2^+ + 2\ N_2 \longrightarrow N_4^+ + N_2 \qquad \text{(Equation 12)}$$

$$N_4^+ + H_2O \longrightarrow H_2O^+ + 2\ N_2 \qquad \text{(Equation 13)}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad \text{(Equation 14)}$$

$$H_3O^+ + H_2O + N_2 \longrightarrow (H_2O)_2\ H^+ + N_2\ . \qquad \text{(Equation 15)}$$

The 60 kev Beta particle ionizes the nitrogen carrier gas, and clustering occurs with neutral nitrogen molecules to form N^+_4. Equation 13 is an oxidation process and is followed by hydride abstraction (equation 14) and nucleophilic attachment (equation 15). Further reactions can occur, depending on the character of the carrier and sample gas. Positive ion clusters of water

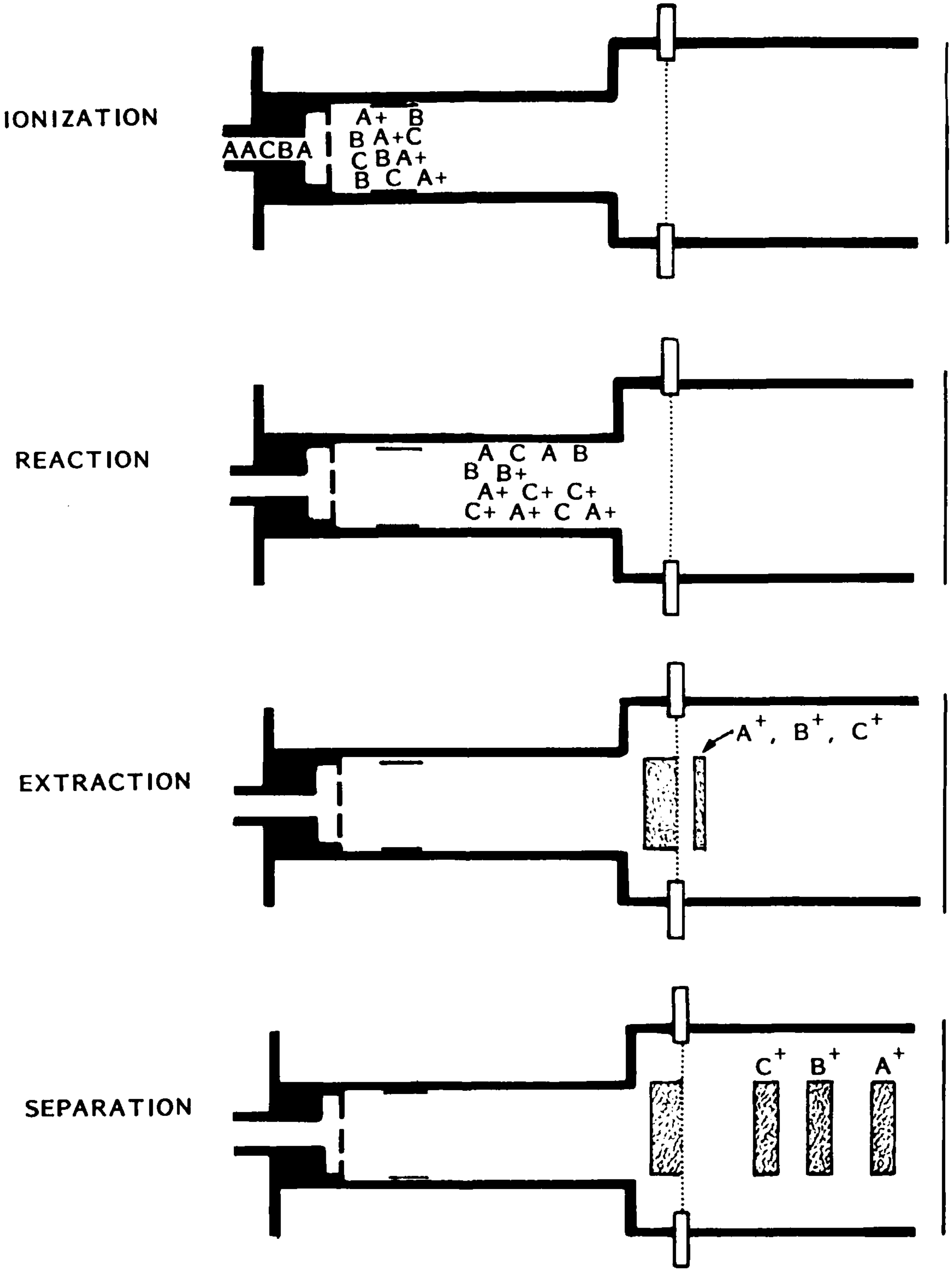


Figure 3. Operation of IMS

with NH^+_4, NO^+, and N_2 have been observed in recent studies.[19] The reactions in equations 11 to 15 proceed quickly to form the protonated water clusters, which generally are the predominant reactant peak observed in IMS. Increased water vapor concentrations promote higher order water clusters, such as

$$(H_2O)_n\ H^+$$

where n = 1,2,3...6.

The sample molecule, M, is drawn into the IMS and can cluster or accept a proton from the reactant ions if the proton affinity is greater than the reactant ions. Positive product ions are formed by the following mechanisms:

proton transfer $(H_2O)_n\ H^+ + M \longrightarrow nH_2O + MH^+$ (Equation 16)

clustering with water, ammonium nitrogen, etc.

$$(H_2O)_n\ H^+ + M \longrightarrow (n - 1)H_2O + M(H_2O)H^+ \quad \text{(Equation 17)}$$

$$NH_4^+ + M \longrightarrow MNH_4^+ \quad \text{(Equation 18)}$$

$$M + N_2 + (H_2O)H^+ \longrightarrow M(N_2)H^+ + H_2O \quad . \quad \text{(Equation 19)}$$

At higher concentrations, sample molecules can form dimers:

$$2M + (H_2O)_n H^+ \longrightarrow n(H_2O) + M_2H^+ \quad . \quad \text{(Equation 20)}$$

The mechanisms for negative reactant ion formation are summarized by Spangler and Collins[20] and include the following reactions:

$$e^-(\text{thermal}) + O_2 \longrightarrow O_2^- \quad \text{(Equation 21)}$$

$$O_2^- + CO_2 \longrightarrow CO_2.O_2^- \quad \text{(Equation 22)}$$

$$O_2^- + nH_2O \longrightarrow (H_2O)_n\ O_2^- \quad \text{(Equation 23)}$$

where n = 1,2.

Clustering of sample molecules with O_2^- reactant ions results in molecular ions to form

$$M + O_2^- \longrightarrow (M)O_2^- \quad . \quad \text{(Equation 24)}$$

Also, a three-body reaction with $CO_2 \cdot O_2^-$ can occur to form CO_2 and MO_2^- clusters.

5. INSTRUMENTATION

A PCP, Inc. MMS-290, which consists of a tandem ion mobility spectrometer and quadrapole mass spectrometer was used for determining mobilities and mass spectra. The system shown in figure 4 consists of the mobility spectrometer, mass spectrometer, Nicolet signal averager, computer, and X-Y recorder. The data generated by the IMS or mass spectrometer are stored in the signal averager for the number of IMS or mass scans specified. Typically, 2,048 scans are made in the IMS or mass spectrometer to improve signal strength and improve the signal-to-noise ratio. The computer stores the collected data on a magnetic disc and controls the timing circuitry in the system. The computer also provides data output on an X-Y plotter, graphics display, or printer and automatically calculates the reduced mobility or ion mass.

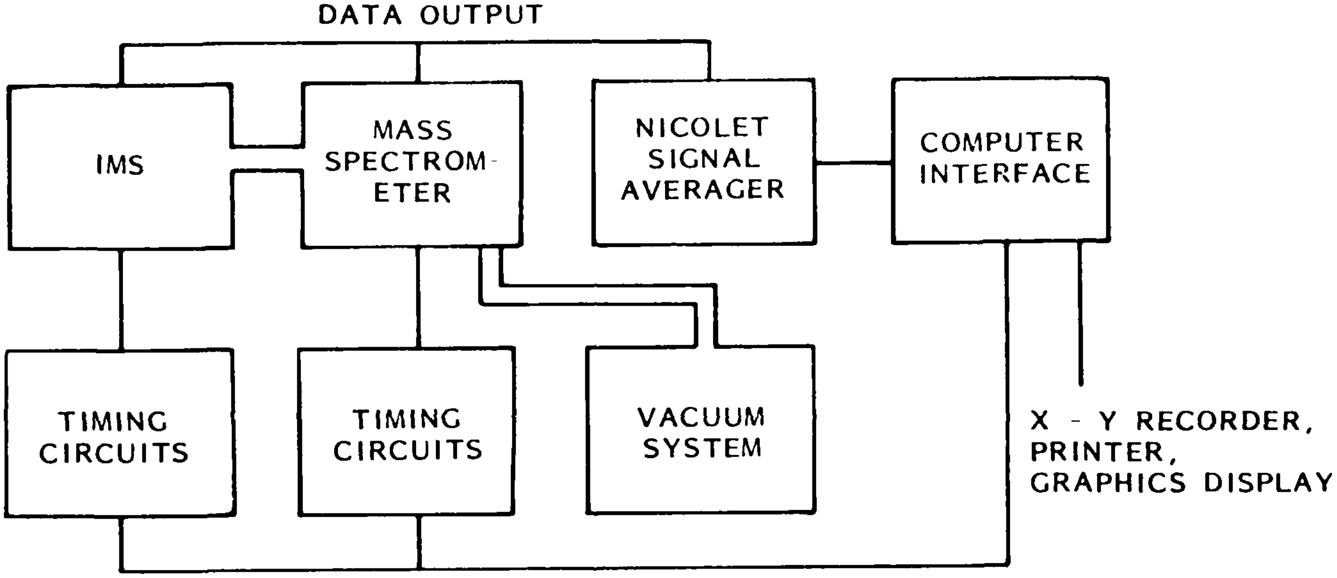


Figure 4. MMS - 290

The MMS-290 can be operated in four distinct modes. The first mode is the total ion or electrometer scan. In this mode the MMS-290 operates as an ion mobility spectrometer. Ions are gated into the drift region and detected by the electrometer. The drift time of each group of ions is averaged, stored, and displayed. All ions traversing the drift region and reaching the electrometer are recorded. The second mode is the integral ion mode and, essentially, is the same as the electrometer mode, except the detector in the mass spectrometer is used as the detector of all ions. The filtering voltages are removed from the quadrapole mass spectrometer, and all ions "leaking" into the mass spectrometer are recorded. This mode is essential to verify that the additional distances that the ions travel during mass spectrometer analysis do not change the distribution of ions and the mobility of the ions. The third mode is the mass spectrum. The shutter grid in the mobility spectrometer is held open continously to allow a steady stream of ions to be "leaked" into the mass spectrometer for detection. All ions formed are recorded by mass scan. The final mode is the tuned ions, which is similar to the integral ion mode except the mass spectrometer is switched to single ion operation. The filtering voltages on the quadrapole mass spectrometer are set to accept only a certain mass, and the shutter grid is gated open continuously.

6. EXPERIMENTAL

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	100°C
Pressure	Entered daily
Drift distance	10 cm

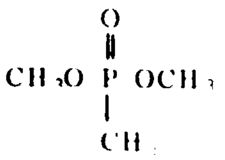
The mobility spectrometer was operated at atmospheric pressure, and the mass spectrometer was operated at 8 X 10^{-5} torr. A controlled vacuum at 700 cc/min was drawn on the gas output of the IMS, and drift gas was supplied at a controlled 500 cc/min. All data reported were subjected to three-point curve smoothing operations which improve signal-to-noise ratio. Mobilities are reported as reduced mobility, K_0. Between daily operations, the IMS was operated overnight at elevated temperatures (≈ 200°C) with clean filtered air to bake out any materials used during the experiments. Each morning a series of positive and negative background spectra were recorded to insure repeatability of reactant ions in the IMS.

The background air (carrier and drift gases) was cleaned and dried through a zero air generator, which reduces the water vapor concentration to 20-30 ppm and removes oils and organics prior to use in the MMS-290. The air capacity of the zero air generator was 20 liters/min with the excess air vented. All metal tubing and glassware were cleaned and vacuum baked prior to use. The interconnecting gas lines were heated to 30°C using electrical cloth resistive heaters to prevent condensation of vapors during transport to the MMS-290.

The samples used for this experiment were:

Dimethyl Meth[illegible]onate (DMMP), $C_3H_9PO_3$	
Molecular Wei[illegible]	[illegible]mu
Vp	[illegible]nm Hg at 24°C
Boiling Point	[illegible]t 10 mm Hg
Density	[illegible]7 g/ml at 20°C

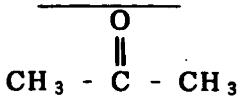
Structure



$CH_3O-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}-OCH_3$

Acetone, C_3H_6O
Molecular Weight = 58 amu
Vp = 400 mm of Hg at 39.5°C
Boiling Point = 56.8°C
Density = 0.8200 g/ml at 21°C

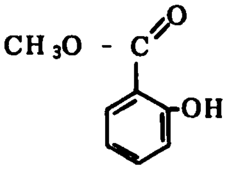
Structure



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Methyl Salicylate (2-hydroxy benzoic acid, methyl ester), $C_8H_8O_3$
Molecular weight = 152 amu
Vp = 1 mm of Hg at 54°C
Boiling Point = 223.3°C (760 torr)
Density = 1.184 g/ml at 20.2°C

Structure



The DMMP, technical grade, was obtained from Mobil Oil Co., and was vacuum distilled at 4 torr to remove phosphite and other impurities. The acetone was ACS grade from laboratory stock. The methyl salicylate was obtained from laboratory supplies and was of unknown purity.

The DMMP and methyl salicylate vapors were generated using a gas dilution apparatus. A small amount of air (about 1-2 ml) was passed over the liquid and vapors of the compound were mixed with the air. The air/vapor mixture was then diluted with a large quantity of clean air. The vapor pressure (of each compound sample), air flow, and dilution air flow were recorded and used to qualitatively estimate the vapor concentrations. The acetone was generated using a Dynacalibrator permeation tube vapor generator. The permeation rates of the acetone permeation tubes were quantatively calibrated using weight loss as a function of temperature and time. The vapor output of the gas dilution device and Dynacalibrator were mixed in a baffle chamber for the mixture studies. All vapor data reported were taken after the concentrations of each compound had reached equilibrium (usually 30 minutes).

7. RESULTS

7.1 Reactant Ions.

Background spectra were taken prior to each day's work to verify air reactant ion repeatability. Positive and negative electrometer spectra and mass spectra for backgrounds are shown in figures 5 through 8. Figure 5 is the positive electrometer spectra on four different days. The range of reduced mobilities is 2.12 to $2.20 \frac{cm^2}{V\ Sec}$ with a few minor peaks shown. The third spectra from the X-axis has a mobility peak at $1.17 \frac{cm^2}{V\ Sec}$ due to some contaminant in the system of unknown origin. Figure 6 is a typical mass spectra in the positive mode showing the masses of molecular ions of air and water clusters. Note that the accompanying data show relative intensity of mass peaks. Figures 7 and 8 are typical mobility and mass spectra of backgrounds.

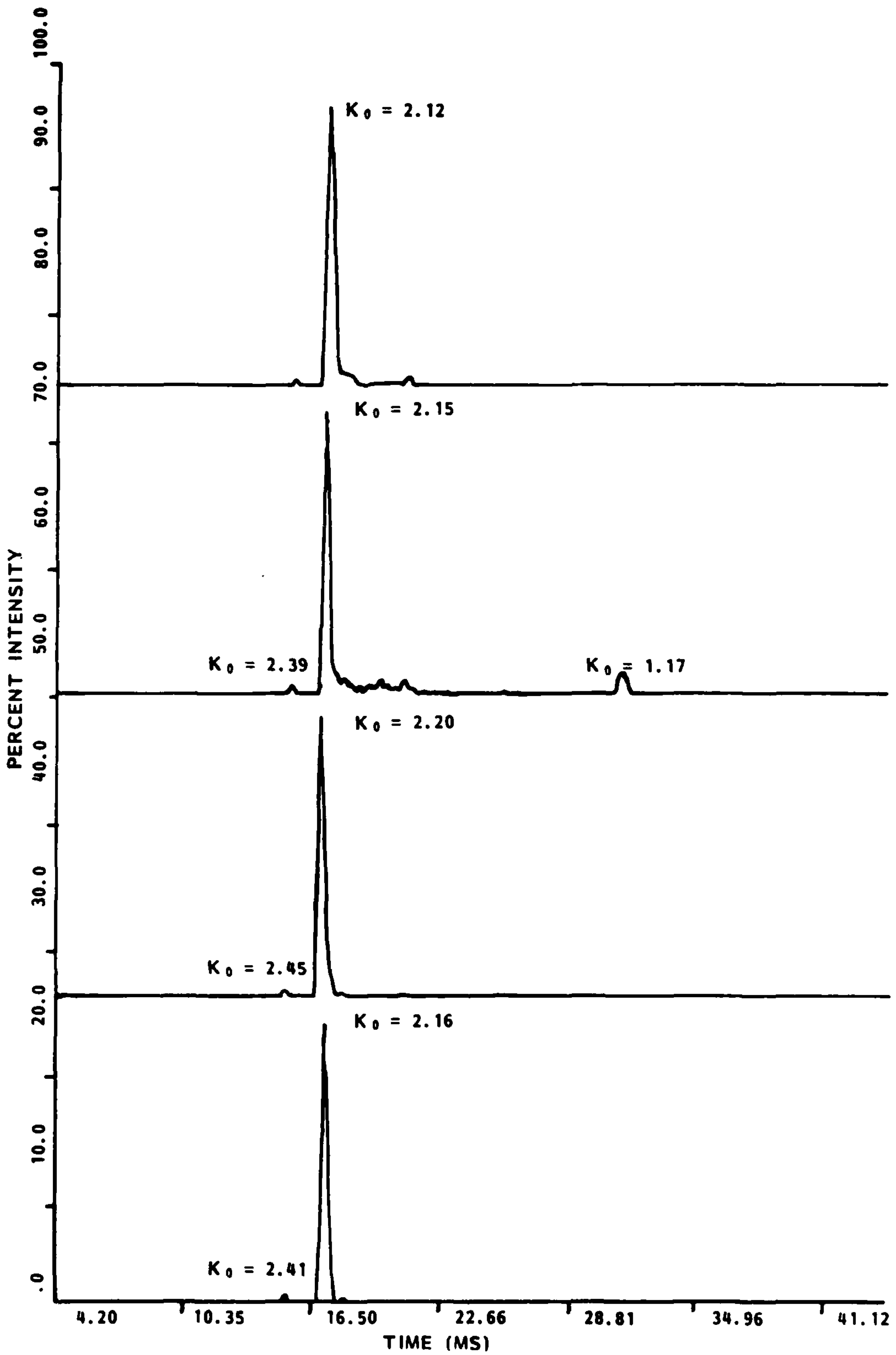
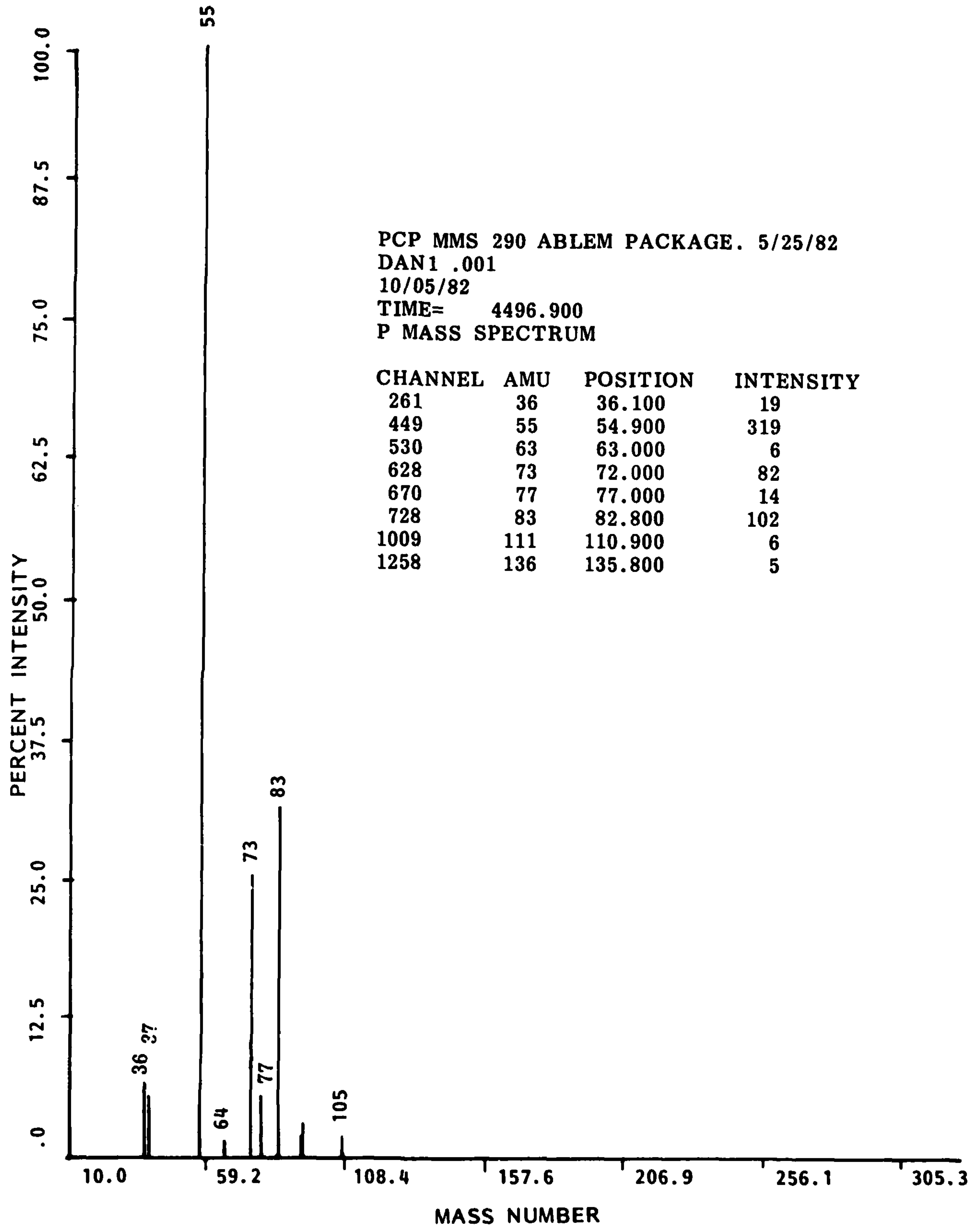


Figure 5. Positive Reactant Ion Mobility



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10/05/82
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  449     55    54.900      319
  530     63    63.000        6
  628     73    72.000       82
  670     77    77.000       14
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 1009    111   110.900        6
 1258    136   135.800        5
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Figure 6. Positive Reactant Mass Spectrum

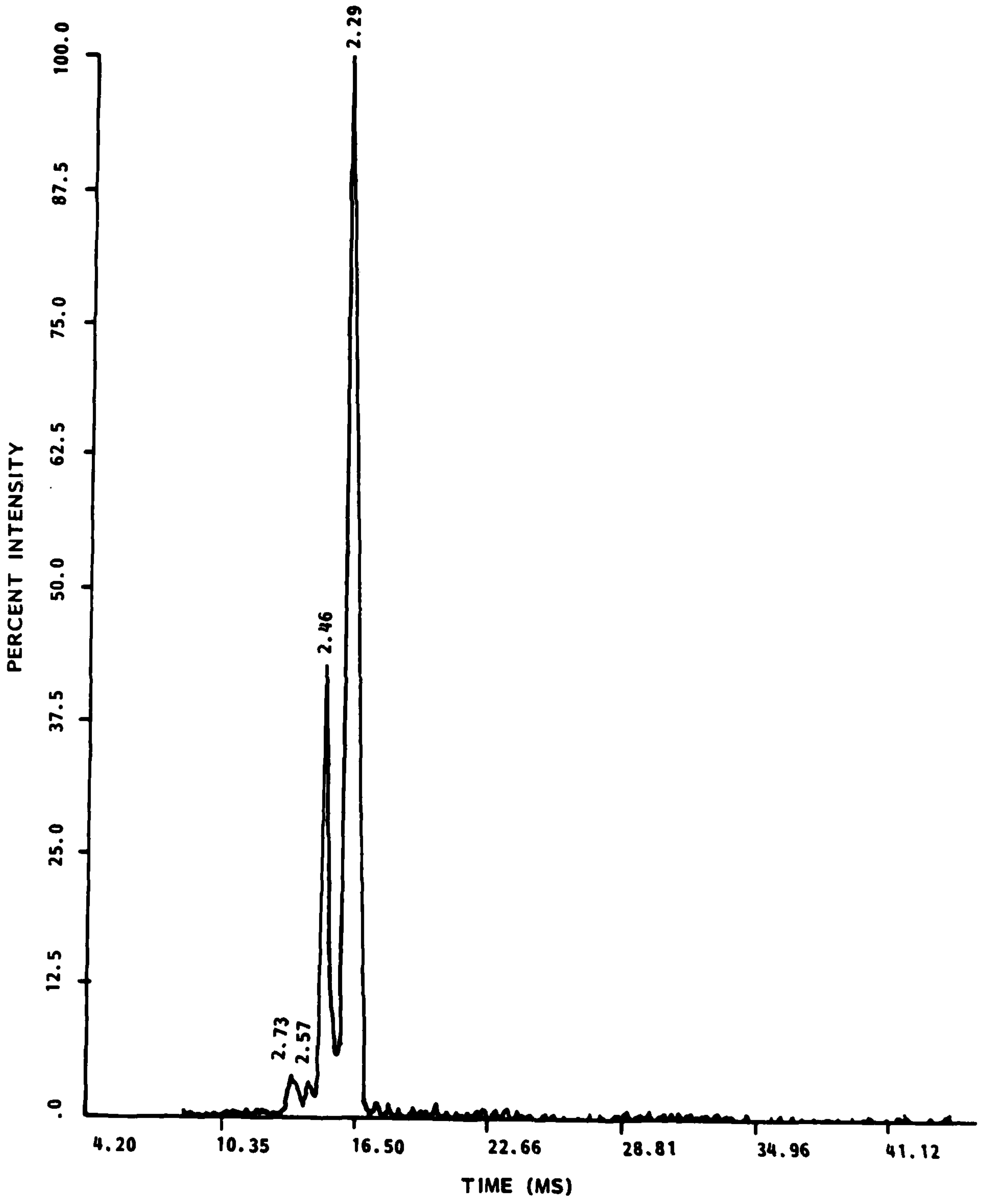
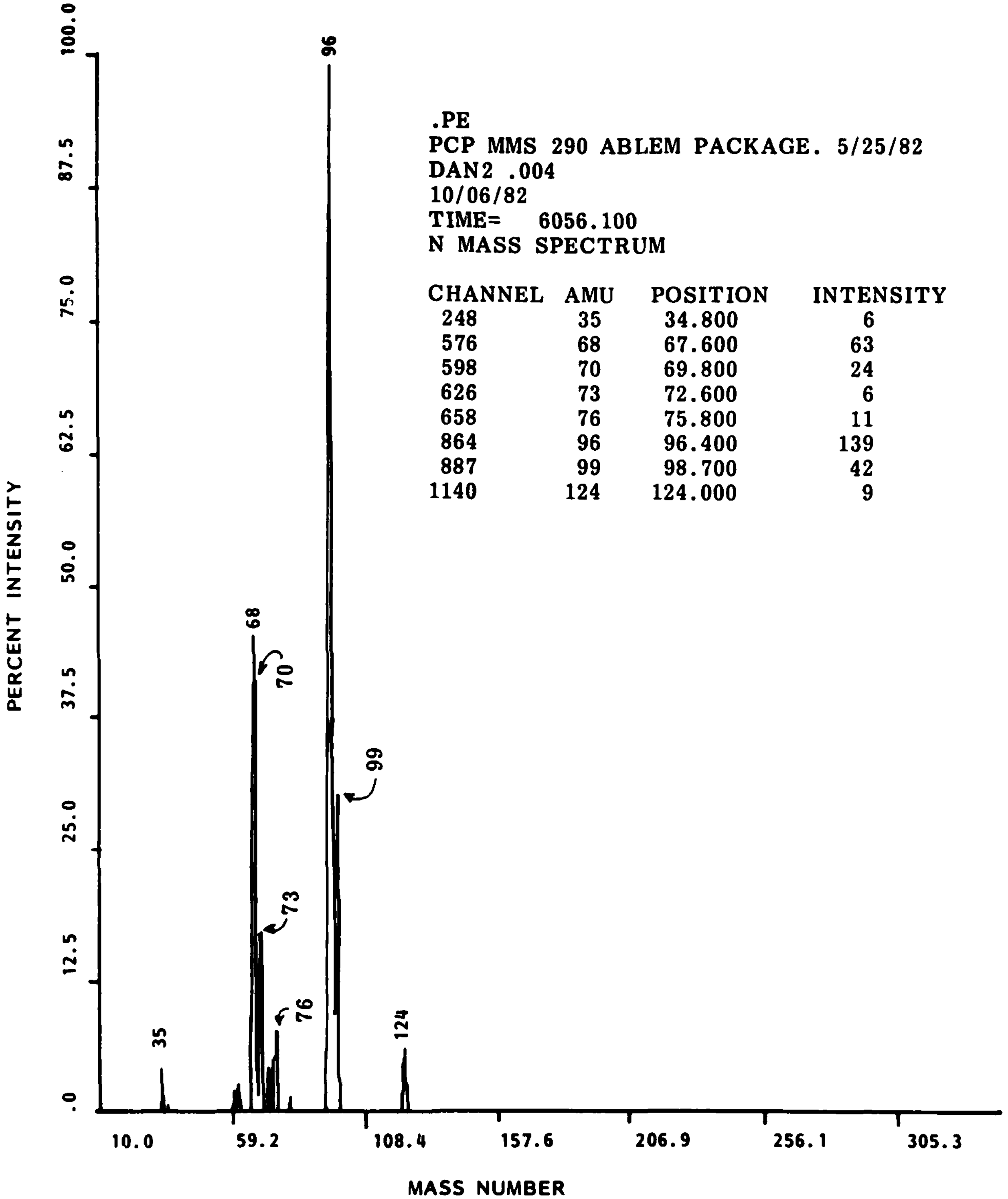


Figure 7. Negative Reactant Ion Mobility (Peak Values are K_0)



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 626      73    72.600        6
 658      76    75.800       11
 864      96    96.400      139
 887      99    98.700       42
1140     124   124.000        9
```

Figure 8. Negative Reactant Mass Spectrum

For each molecular ion in the mass spectra, a series of tuned ion spectra were run using the mass spectrometer to identify the molecular ions contributing to a specific mobility peak. A summary of the major ion masses conributing to the positive mobility peaks is given in table 1, and in table 2 the negative ions and mobilities as well as the probable clusters are given.

Table 1. Positive Reactant Ions

$K_0 = 2.40$		$K_0 = 2.20$ to 2.12		$K_0 = 1.17$	
amu	ion	amu	ion	amu	ion
36	$(H_2O)NH_4^+$	37	$(H_2O)_2H^+$	278	Unknown
64	$(H_2O)(N_2)NH_4^+$	55	$(H_2O)_3H^+$		
		73	$(H_2O)_4H^+$		
		83	$(H_2O)_3N_2H^+$		
		111	$(H_2O)_3N_4H^+$		

In table 1 the major mobility peak is at 2.12 to 2.20 $\frac{cm^2}{V\ Sec}$ and is a contribution of protonated water clusters and nitrogen. The probable mechanisms are

$$(H_2O)H^+ + nH_2O \rightleftharpoons (H_2O)_{n+1}H^+ \quad ;$$

a three-body reaction involving nitrogen,

$$(H_2O)H^+ + N_2 + nH_2O \rightleftharpoons (H_2O)_{n+1}(N_2)H^+ \quad ,$$

and

$$(H_2O)H^+ + 2N_2 + n(H_2O) \rightleftharpoons (H_2O)_{n+1}(N_2)_2H^+ \quad .$$

Note that at least five molecular ions have a mobility of near 2.16. This seems in conflict with the goal of the IMS system. These identical mobilities are due to a dynamic equilibria occurring in the dirft region of the IMS. The proton affinity is nearly identical for water clusters involving 1, 2, and 3 water molecules. Similiar data were reported by Karasek et al[8] for

$$(H_2O)_nH^+ + N_2 \rightleftharpoons (H_2O)_nN_2H^+$$

where ion masses 37 and 65 had the same mobility.

The two major negative mobility peaks are given in table 2, and the probable contributing ions are shown. The 76 amu has previously been identified by Spangler and Collins with a reduced mobility of 2.41 $\frac{cm^2}{V\ Sec}$. The negative mass spectra shows additional ions at molecular weights of 35, 70, 73, and 99 amu. The 35, 70, and 73 amu are probably chlorine 35 and isotopic chlorine 37. The 73 amu may be inaccurate by a few tenths of an amu, and other negative mass spectra gave a 70- and 74-amu mass, which would be $^{35}Cl_2^-$ and $^{37}Cl_2^-$. The 99 amu is an unknown ion but does not involve chlorine since an ion 2 amu higher for the 37 chlorine isotope is not evident. The source of the chlorine in the mass spectra was unknown and varied with each days operation.

Table 2. Negative Reactant Ions

$K_0 = 2.46$		$K_0 = 2.29$	
amu	Ion	amu	Ion
68	$(H_2O)_2O_2^-$	96	$(H_2O)_2CO_3^-$
76	$CO_2{\cdot}O_2^-$	124	$(H_2O)_2(N_2)O_2^-$

7.2 DMMP.

DMMP was generated using the gas dilution generator at an estimated concentration of 0.5 parts per billion (ppb). The positive mobility spectra of DMMP shows two additional mobility peaks with drift times greater than the reactant mobility peak. Figures 9 and 10 are the positive mobility spectra of DMMP with the tuned ions shown above the total ion mobility. Figure 9 shows that the reactant peak at 2.13 $\frac{cm^2}{V\ Sec}$ is due to 55, 73, and 83 amu, which are $(H_2O)_3H^+$, $(H_2O)_4H^+$, and $(H_2O)_3\ N_2H^+$, respectively. Figure 10 shows two mobility peaks at K_0 of 1.82 and 1.37. Tuned masses at 125, 143, and 153 amu gave a reduced mobility of 1.82 and are postulated as $(DMMP)H^+$, $(DMMP)(H_2O)\ H^+$, and $(DMMP)\ N_2H^+$ clusters. The 249-amu ion has a mobility of 1.37 and is the protonated dimer of DMMP. The mechanism for DMMP involves proton transfer and clustering reactions that are of the form

$$(H_2O)_nH^+ + DMMP \rightleftharpoons (DMMP)H^+ + n(H_2O)$$

$$n(H_2O) + (DMMP)H^+ \rightleftharpoons (DMMP)(H_2O)H^+ + n\text{-}1(H_2O)$$

$$N_2 + (DMMP)H^+ \rightleftharpoons (DMMP)N_2H^+ \quad .$$

Note that the first reaction proceeds to form the protonated monomer. The DMMP has a higher proton affinity than the water clusters and the reaction goes to completion. This hypothesis is supported by the decrease of water

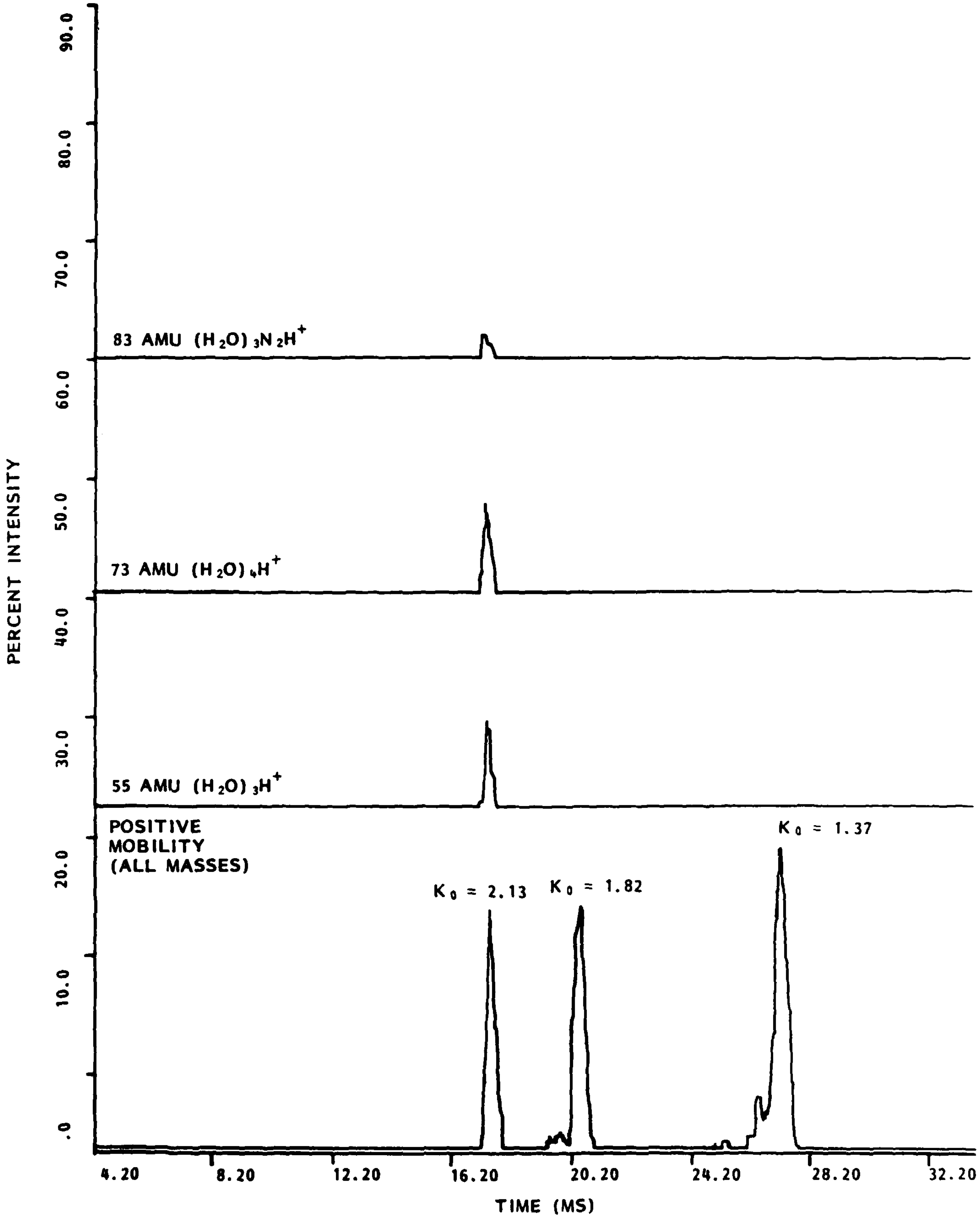


Figure 9. Tuned Ion, Positive Mobility, DMMP, 0.5 ppb

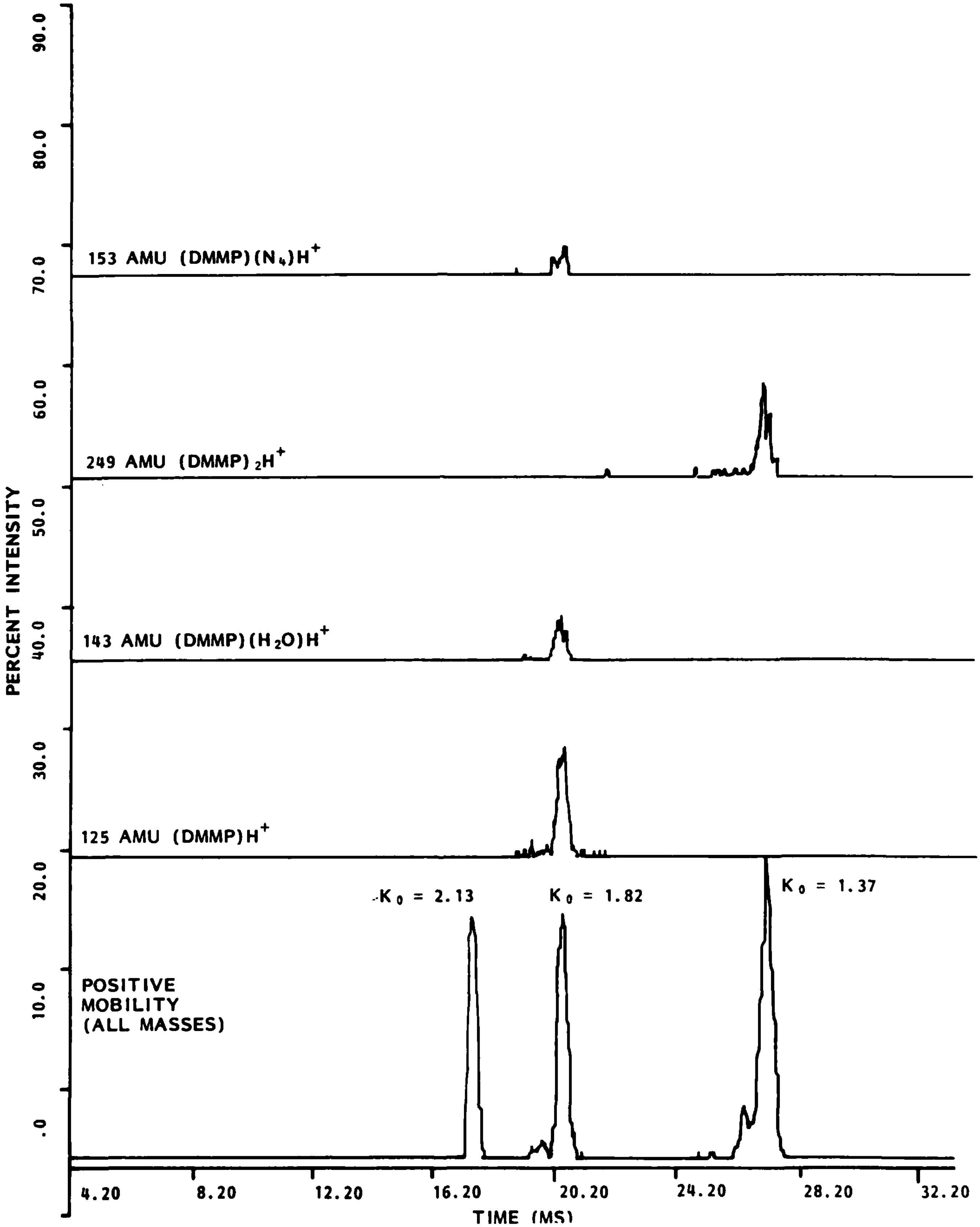


Figure 10. Tuned Ion, Positive Mobility, DDMP, 0.5 ppb

cluster concentrations in the positive mass for DMMP (figure 11). The dimer of DMMP is formed by the following mechanism:

$$(H_2O)_nH^+ + 2DMMP \longrightarrow (DMMP)_2H^+ + nH_2O \quad .$$

This reaction, like the monomer, goes to completion, and the prevelence of the dimer peak is a function of DMMP concentration. The proposed mechanism does not involve $(DMMP)H^+$ since a reaction involving $(DMMP)H^+$ would be reversible and, therefore, they would have identical mobilities.

The negative mobility and mass spectra for DMMP were unchanged from the background spectra, indicating that DMMP does not form negative ions at the experimental conditions. Figure 12 is the tuned negative masses contributing to the negative mobility spectrum.

7.3 Acetone.

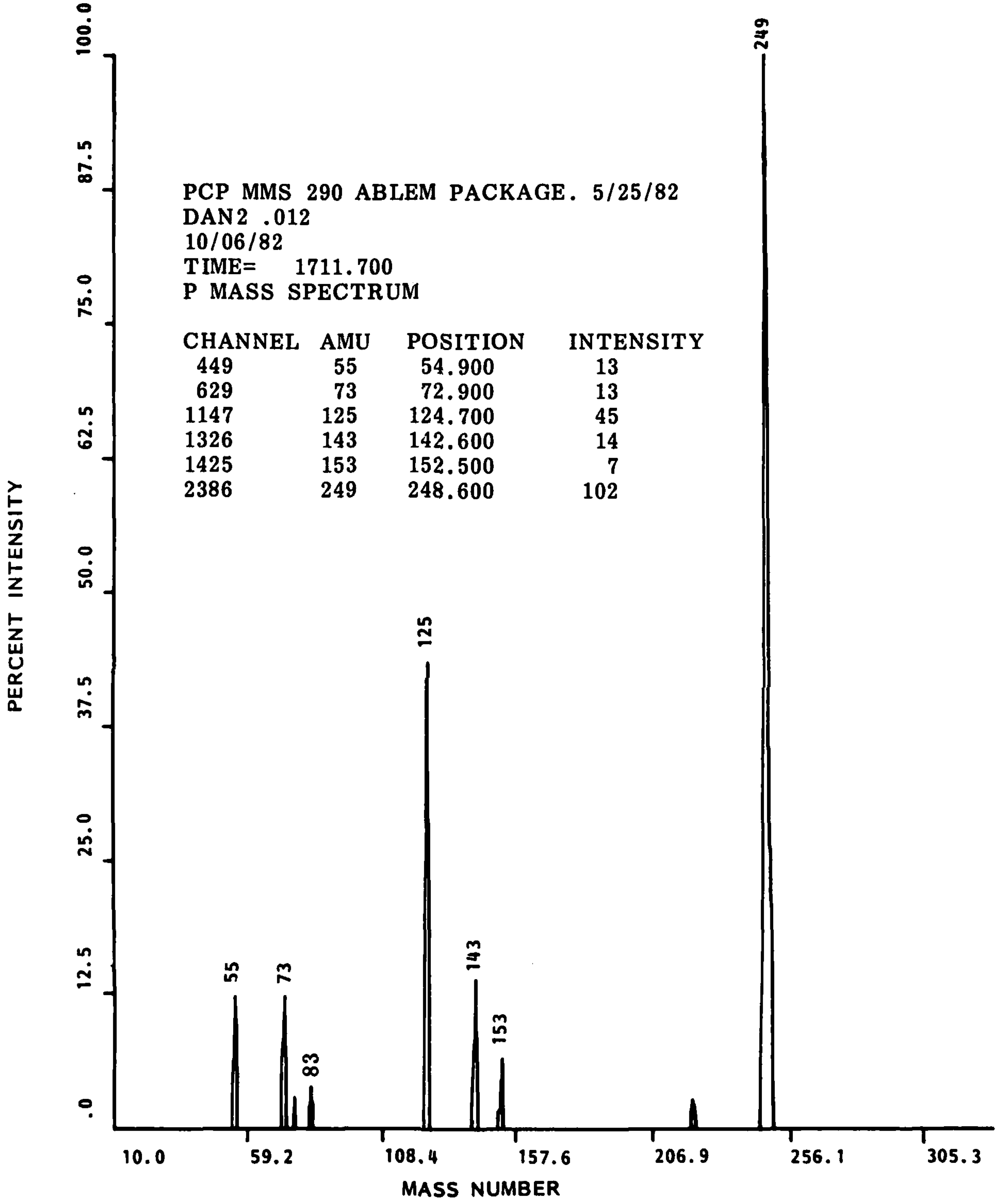
The effects of acetone on the mobility of DMMP were determined. First the positive mass spectrum (figure 13) and mobility spectrum (figure 14a) of acetone were determined. The acetone concentration was estimated to be 81 ppb. The positive mass spectrum has one major peak at 117 amu, which is the protonated acetone dimer $(C_3H_6O)_2H^+$. The background reactant ions do not appear in the mass spectrum, indicating that the acetone molecule has a much greater proton affinity than air and water clusters. The mobility spectrum (figure 14a) is a single, sharp peak at 1.82, and the air reactant peaks are completely gone ($K_0 = 2.13$). The negative mass and mobility spectra for acetone were unchanged from the negative background and are not shown.

7.4 DMMP/Acetone.

Vapors of DMMP at 0.5 ppb were thoroughly mixed with 81 ppb of acetone and the mixture drawn into the IMS. The spectrum shown in figure 14b is the mobility spectrum of DMMP and acetone. Note that the acetone mobility is identical (K_0 = 1.82 and 1.84) in both spectra in figures 14a and 14b. The second and third peaks have mobilities of K_0 = 1.70 and 1.38. The mass spectra of DMMP and acetone are shown in figure 15. Note that all ions masses below 117 amu are gone. The major ion masses are 117, 125, 143, and 248 amu and are hypothesized as $(C_3H_6O)_2H^+$, $(DMMP)H^+$, $(DMMP)(H_2O)H^+$, and $(DMMP)_2H^+$. The 248 amu is assumed to be in error by a few tenths of an amu and is the 249 mass which is the DMMP dimer. The 182 and 223 amu masses are unidentified. The tuned masses for the mixture of DMMP and acetone are shown in figure 16 and a summary of the data are given in table 3.

Table 3. Positive Ions of DMMP/Acetone

K_0 = 1.84		K_0 = 1.76 - 1.66		K_0 = 1.37	
amu	ion	amu	ion	amu	ion
117	$(C_3H_6O)_2H^+$	125	$(DMMP)H^+$	249	$(DMMP)_2H^+$
		143	$(DMMP)(H_2O)H^+$		



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PCP MMS 290 ABLEM PACKAGE. 5/25/82
DAN2 .012
10/06/82
TIME=   1711.700
P MASS SPECTRUM

CHANNEL  AMU    POSITION     INTENSITY
 449      55     54.900        13
 629      73     72.900        13
1147     125    124.700        45
1326     143    142.600        14
1425     153    152.500         7
2386     249    248.600       102
```

Figure 11. Positive Mass Spectrum, DMMP, 0.5 ppb

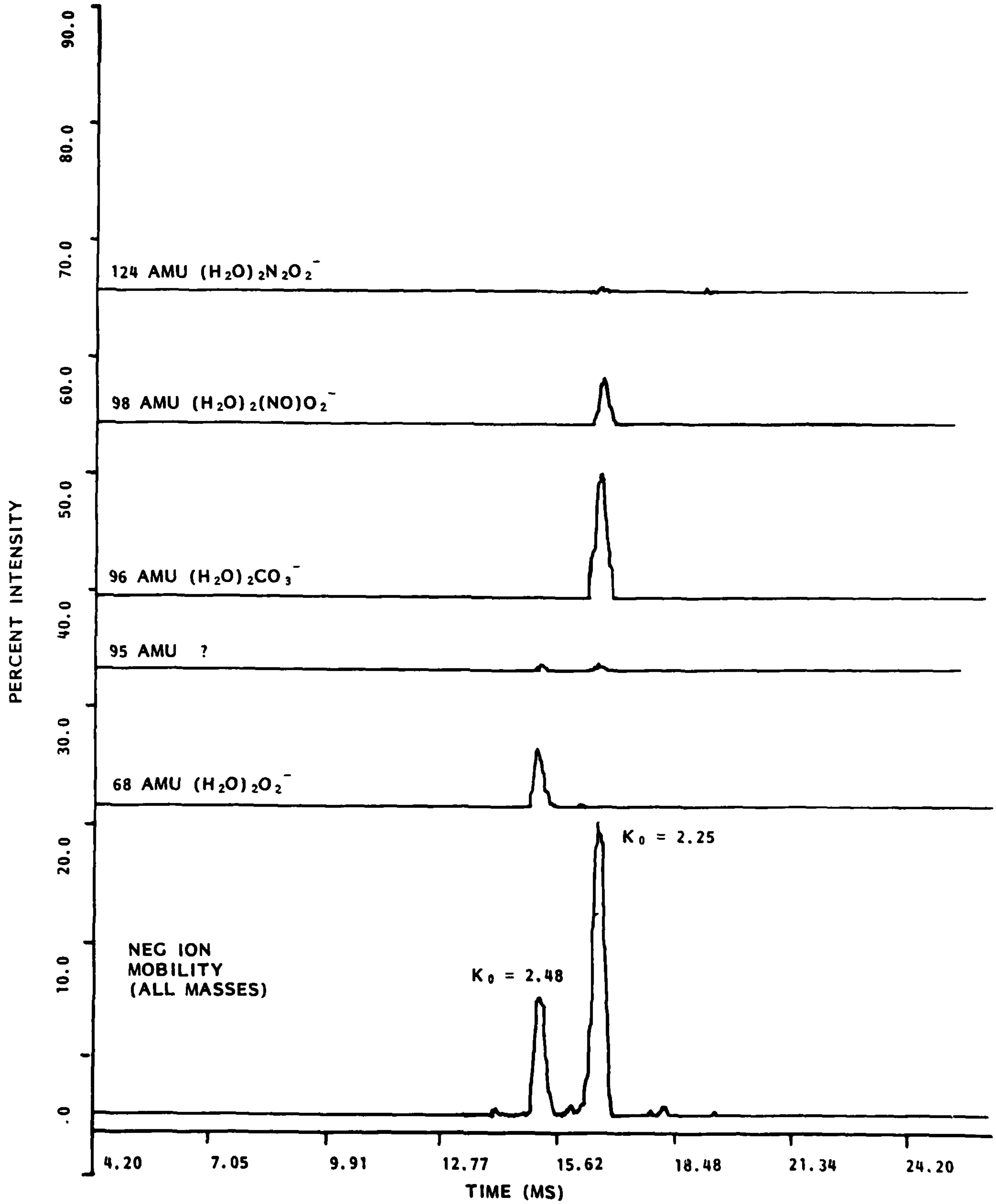
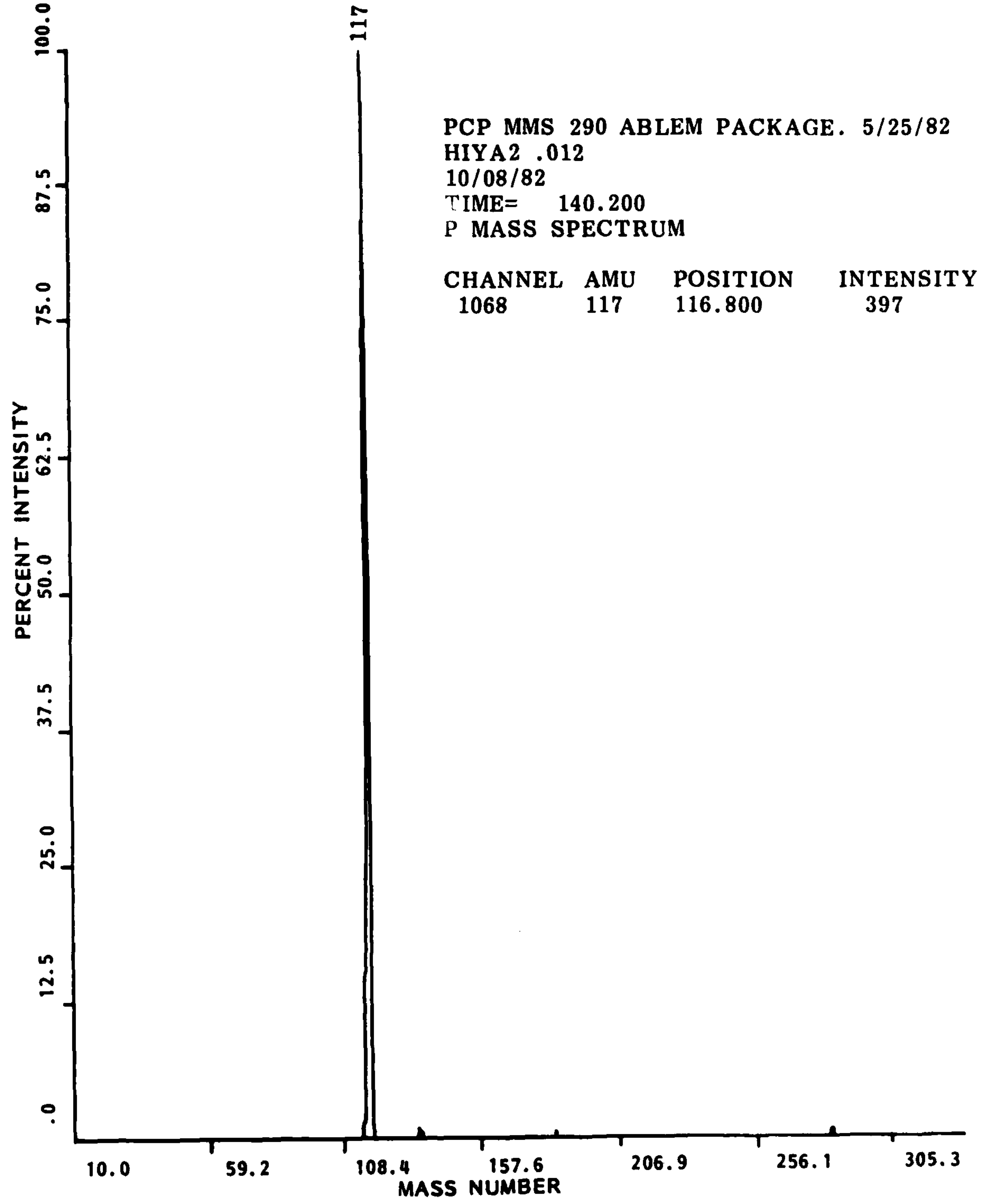


Figure 12. Tuned Ion, Negative Mobility, DMMP, 0.5 ppb



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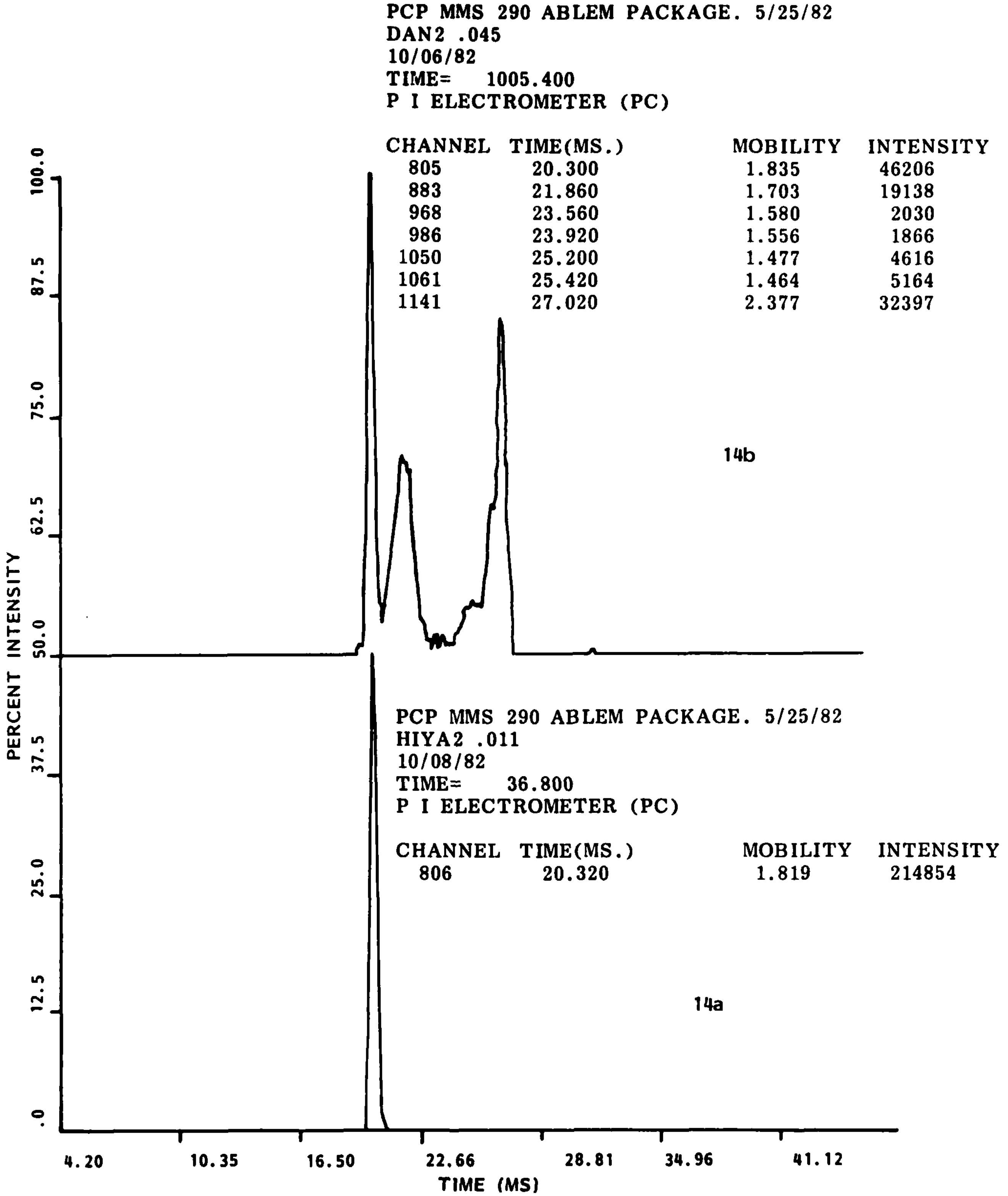
PCP MMS 290 ABLEM PACKAGE. 5/25/82
HIYA2 .012
10/08/82
TIME=   140.200
P MASS SPECTRUM

CHANNEL  AMU   POSITION    INTENSITY
 1068    117   116.800        397
```

Figure 13. Positive Mass Spectrum, Acetone, 81 ppb



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DAN2 .045
10/06/82
TIME=   1005.400
P I ELECTROMETER (PC)

CHANNEL  TIME(MS.)          MOBILITY  INTENSITY
  805      20.300            1.835     46206
  883      21.860            1.703     19138
  968      23.560            1.580      2030
  986      23.920            1.556      1866
 1050      25.200            1.477      4616
 1061      25.420            1.464      5164
 1141      27.020            2.377     32397
```

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PCP MMS 290 ABLEM PACKAGE. 5/25/82
HIYA2 .011
10/08/82
TIME=    36.800
P I ELECTROMETER (PC)

CHANNEL  TIME(MS.)          MOBILITY  INTENSITY
  806      20.320            1.819     214854
```

Figure 14. Positive Ion Mobility: Acetone, 81 ppb (14a); and DMMP, 0.5 ppb and Acetone 81 ppb (14b)

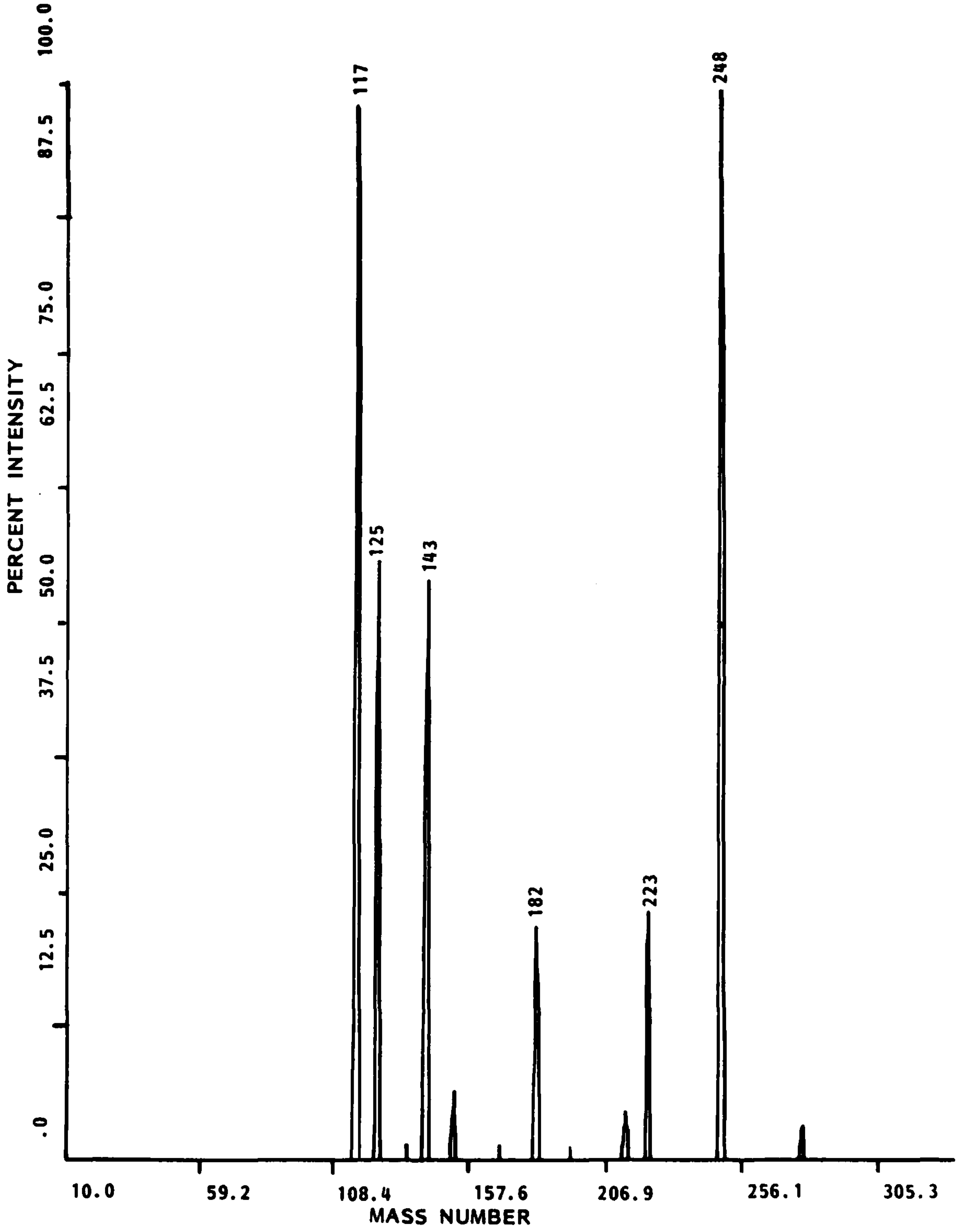


Figure 15. Positive Mass Spectrum, DMMP, 0.5 ppb and Acetone, 81 ppb

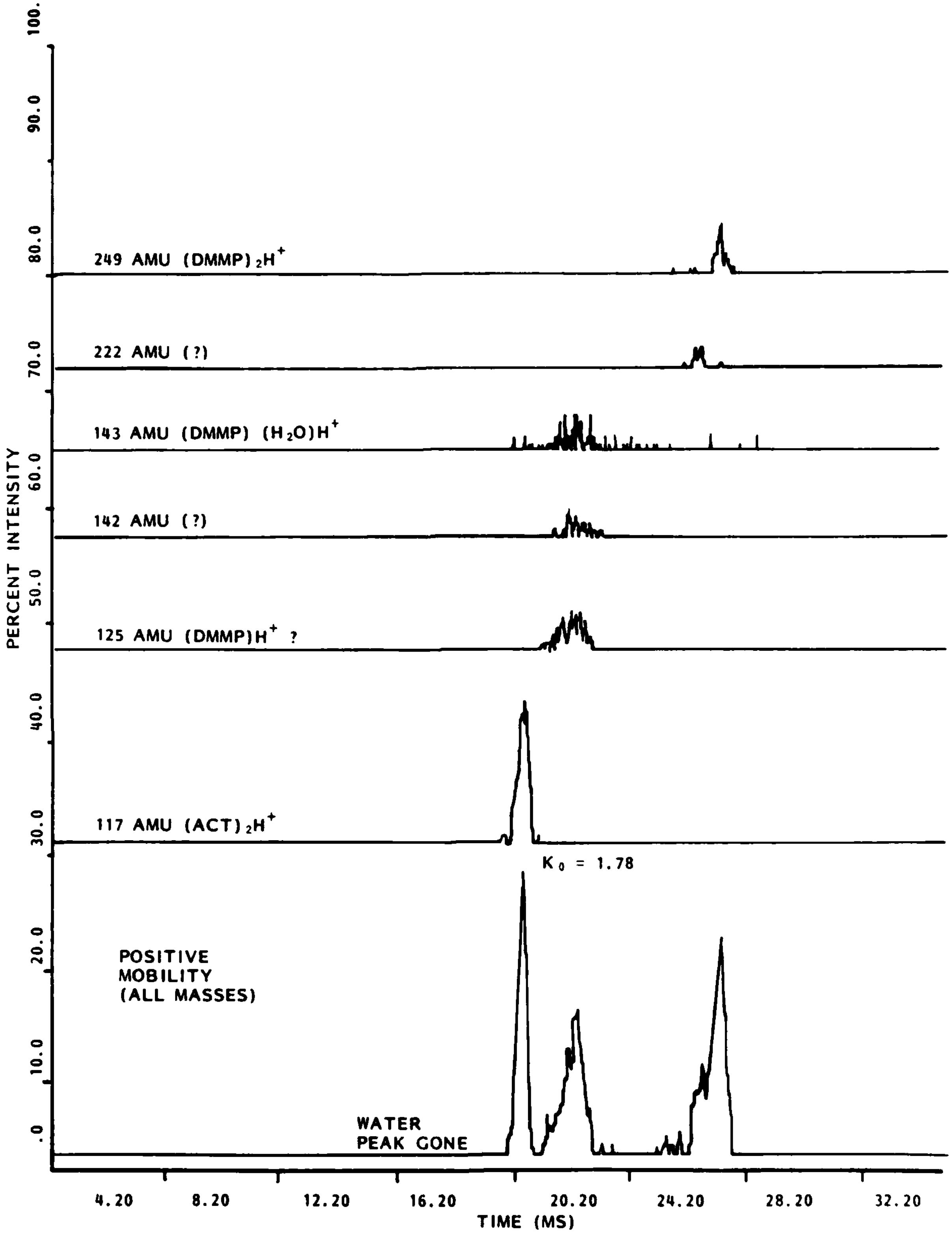


Figure 16. Tuned Ion, Positive Mobility, DMMP, 0.5 ppb, Acetone, 81 ppb

The mobility/ion molecule assignments do not agree with the previous data shown in figure 10. The $(DMMP)H^+$ and $(DMMP)(H_2O)H^+$ had a mobility of $K_0 = 1.82$; yet, when DMMP is mixed with acetone, the monomer and hydrate appear to have a lower mobility ($K_0 \approx 1.76$ to 1.66). The first hypothesis considered was that acetone and DMMP were clustering together to form a 183-amu ion, $(DMMP)(C_3H_6O)H^+$, but the tuned ion at 182 amu showed little contibution to the mobility spectra. The mass spectra does give a 182-amu ion, but this ion does not seem to contribute to the mobility spectrum. Higher resolution mobility and mass spectra are required to test the DMMP/acetone hypothesis and will be the object of future work.

7.5 Methyl Salicylate.

The positive ions formed by methyl salicylate were studied and the data are shown in figures 17 and 18. Methyl salicylate forms a strong positive ion, $(C_8H_8O_3)H^+$. The concentration was 17 ppb. Figure 17 shows the tuned ions for methyl salicylate at masses of 153 and 171, which are hypothesized as $(C_8H_8O_3)H^+$ and $(C_8H_8O_3)(H_2O)H^+$. The mobility of the monomer and hydrate is 1.71. The 279 amu was tuned since it was in the background spectra. The 279 is of unknown origin and does not contribute to the mobility peak at $K_0 =$ 1.17. The 136- and 181-amu ions shown in figure 18 were tuned, but no counts were shown in the mobility spectra. Possibly, the 181 amu could be $(C_8H_8O_3)N_2H^+$. The negative mobility and mass spectra of methyl salicylate were unchanged from the background spectrum and are not shown.

7.6 Methyl Salicylate/Acetone.

A mixture of methyl salicylate and acetone were investigated for mobilities. The methyl salicylate concentration was 17 ppb, and the acetone concentration was 81 ppb. The mobility spectrum is shown in figure 19. Two distinct mobility peaks are shown at $K_0 = 1.82$ and 1.68. The two peaks are attributed to $(C_3H_6O)_2H^+$ and $(C_8O_8O_3)H^+$, respectively. Tuned ions verified that these molecular weights had the assigned mobilities. The mass spectrum of the mixture is shown in figure 20, and the same masses are recorded as for the methyl salicylate, except for the 117 amu of acetone. The negative mobility and mass spectra showed no change from background data and are not shown.

8. CONCLUSION

The data reported for reactant ions show that primary ion formation occurs with $(H_2O)_nH^+$ in the positive mode and $(H_2O)_2O_2^-$; $(H_2O)_2CO_3^-$ in the negative mode. The mobility spectra were repeatable between each day's run and contaminants were effectively removed. Peak assignments for reactants are similar to work done by previous researchers, and the tuned ion spectra verified mass contribution to a particular mobility. The dynamic equilibria of reactant ions in the drift region of the IMS result in mobilities of different mass molecular ions. The extent of identical mobilities for several molecular ions has not previously been reported. The reduced mobility of DMMP was determined to be 1.82 cm^2/Vsec for the protonated monomer and 1.37 cm^2/Vsec for the dimer. The mobility of the acetone dimer was reported as identical to the $(DMMP)^+$ ion, $K_0 = 1.82$ cm^2. A mixture of DMMP and acetone drastically changed the DMMP mobility spectrum. The formation of $(DMMP)H^+$ and $(DMMP)(H_2O)H^+$ and possibly (DMMP)(C_3H_6O)H^+ is suspect in the DMMP/acetone mixture. The effects on the mobility of the DMMP monomer in the presence of acetone will be the object of future work. The previously unreported positive mobility of methyl salicylate was found to be 1.71 cm^2. Mixtures of acetone and methyl salicylate do not affect the distinct mobilities of each compound. Negative ions at the conditions reported do not occur for DMMP, acetone, and methyl salicylate.

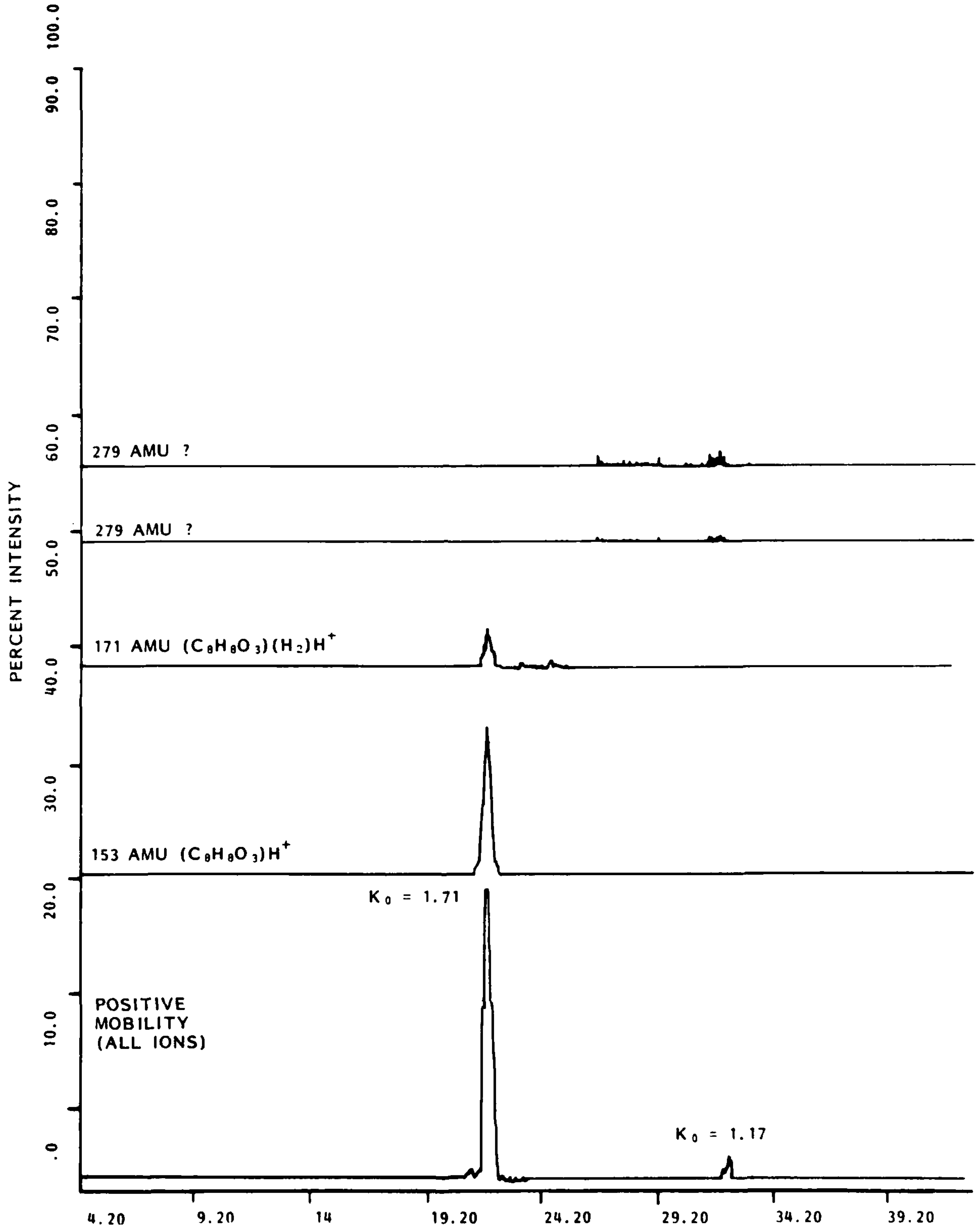


Figure 17. Tuned Ion, Positive Mobility, Methyl Salicylate, 17 ppb

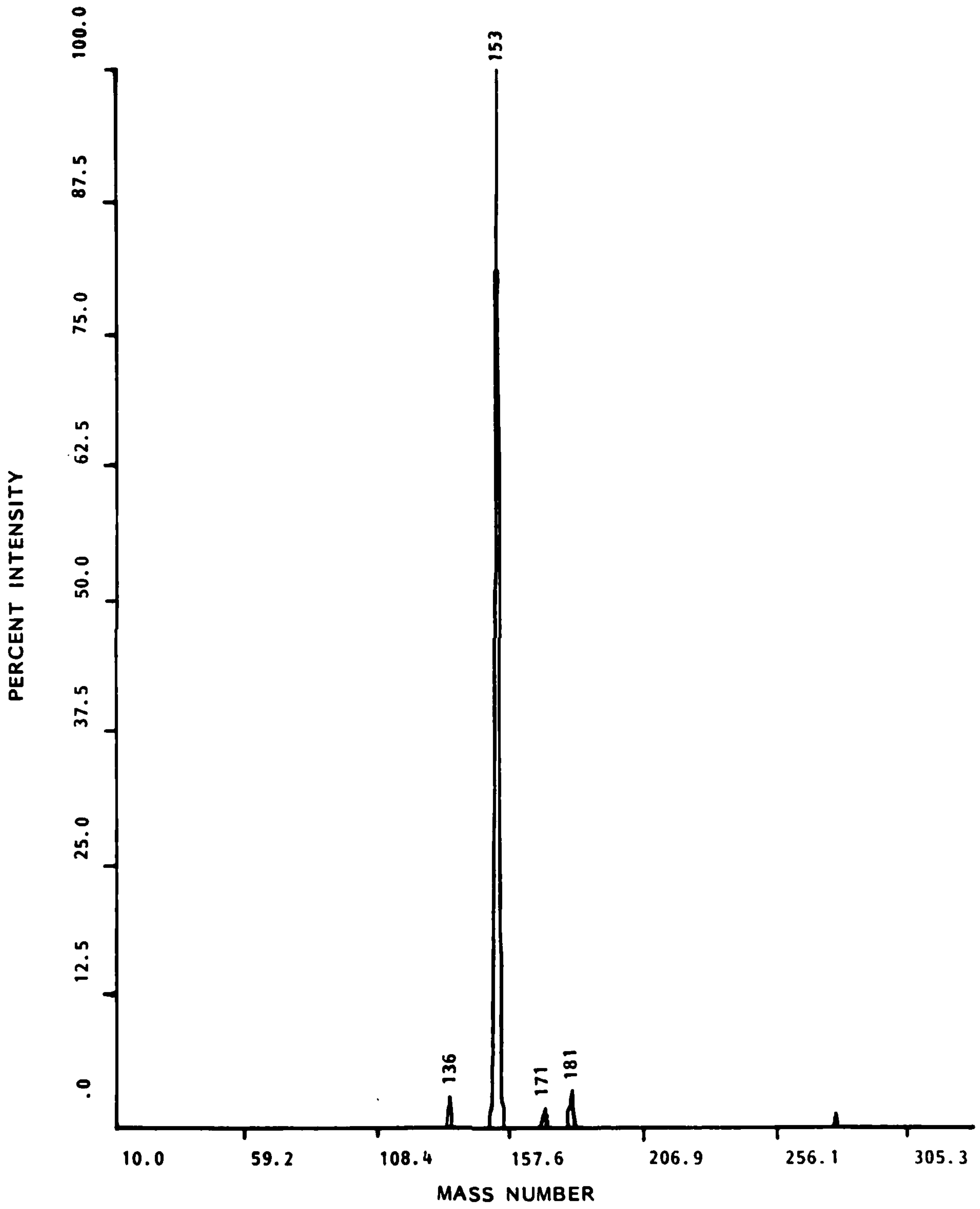


Figure 18. Positive Mass Spectrum, Methyl Salicylate, 17 ppb

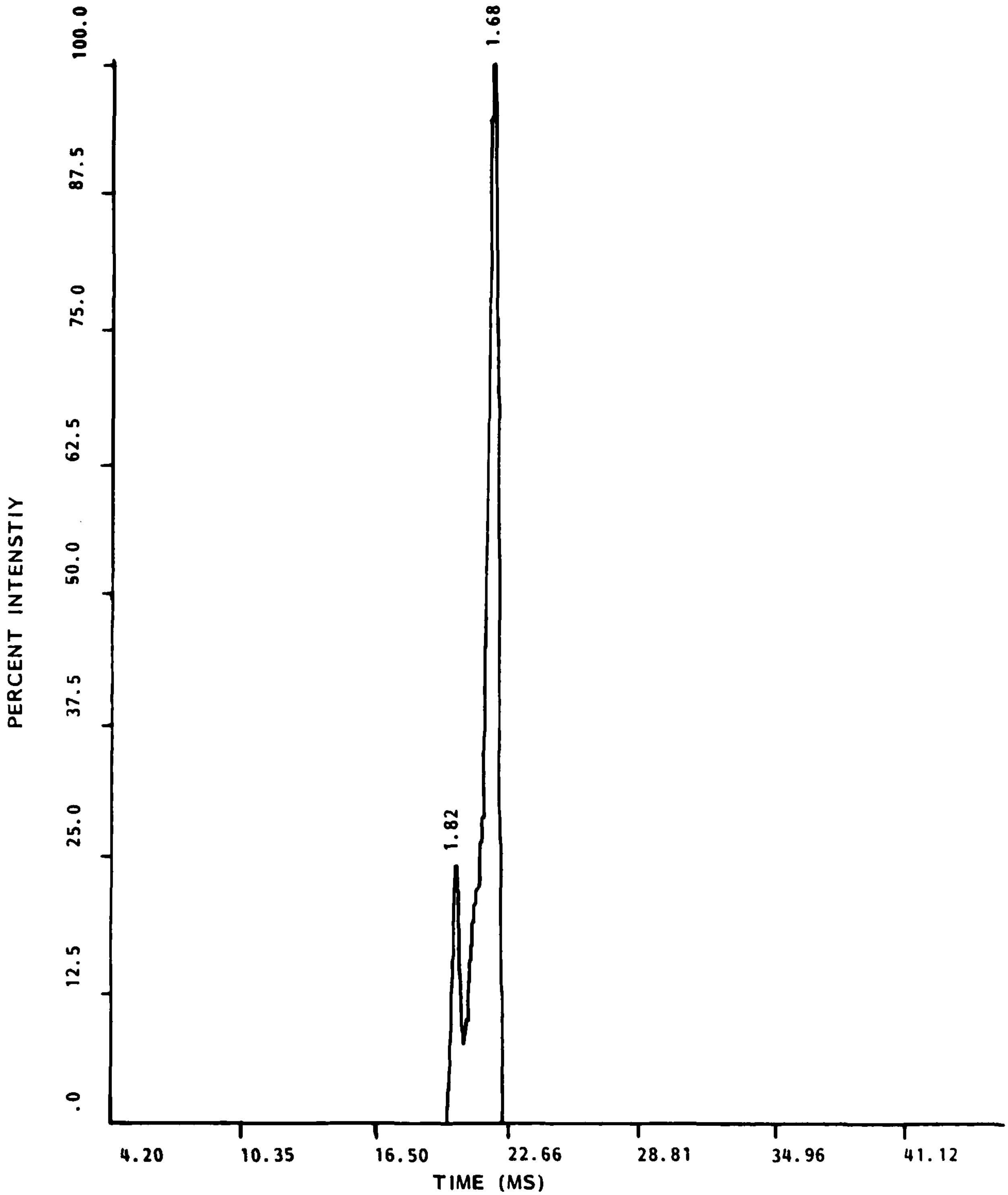
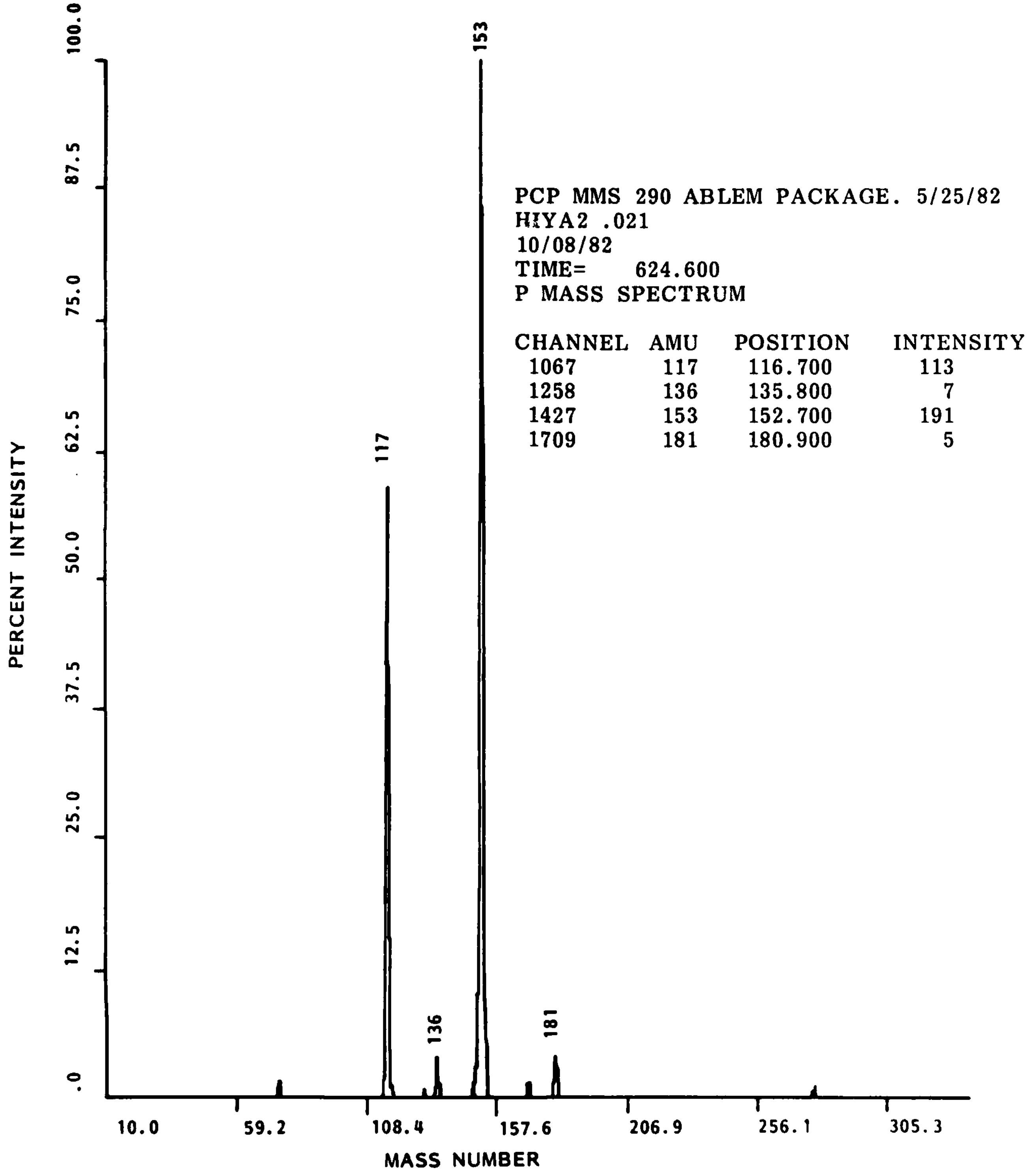


Figure 19. Positive Mobility Spectrum, Methyl Salicylate, 17 ppb and Acetone, 81 ppb



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PCP MMS 290 ABLEM PACKAGE. 5/25/82
HIYA2 .021
10/08/82
TIME=    624.600
P MASS SPECTRUM

CHANNEL  AMU    POSITION    INTENSITY
 1067     117    116.700        113
 1258     136    135.800          7
 1427     153    152.700        191
 1709     181    180.900          5
```

Figure 20. Positive Mass Spectrum, Methyl Salicylate, 17 ppb and Acetone, 81 ppb

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