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APPLICATION OF ION-INDUCED NUCLEATION MASS SPECTROMETRY IN THE ANALYSIS OF TRACE GASES EVOLVED FROM A POLYIMIDE FILM DURING THE THERMAL CURING STAGES
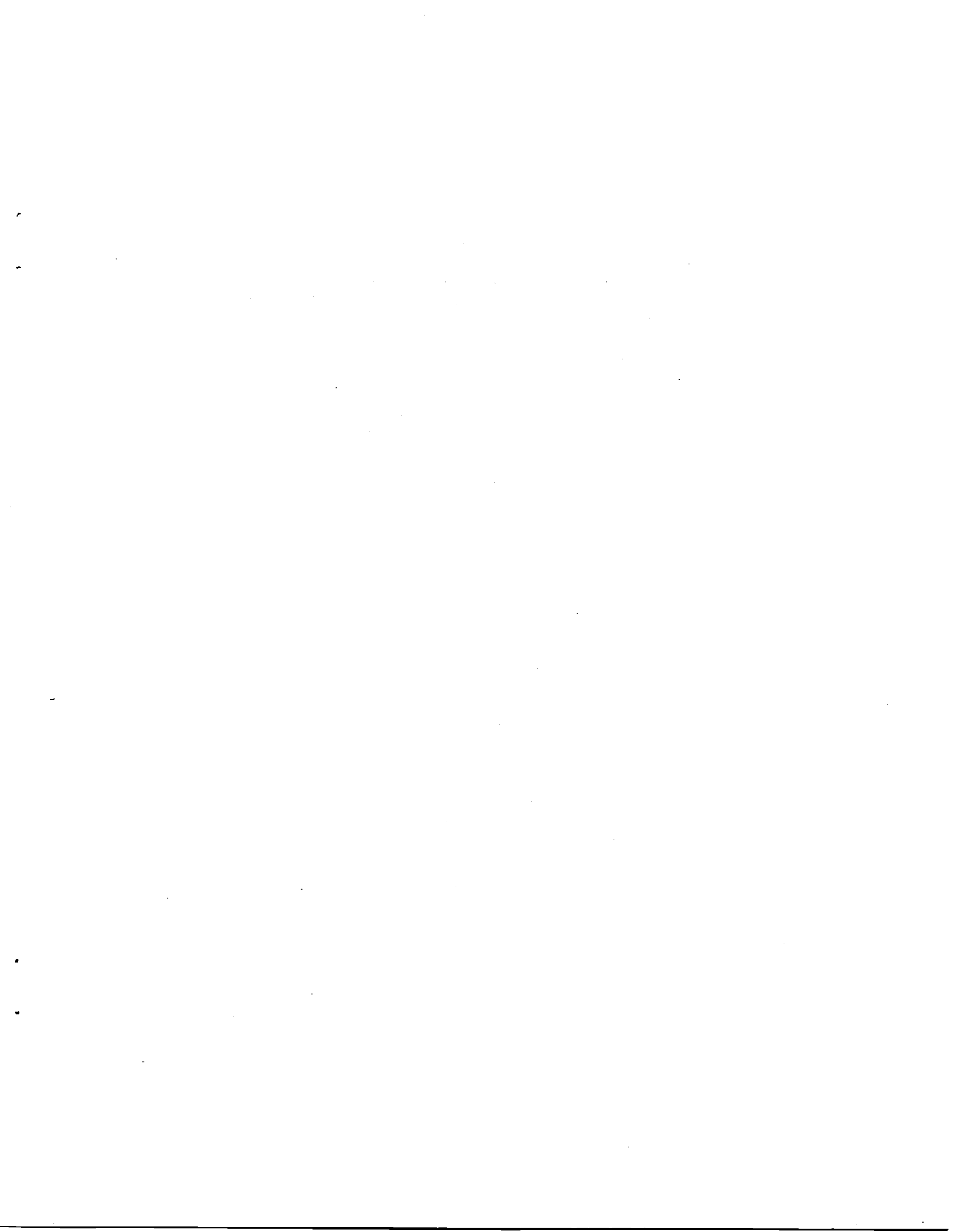
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SUMMARY

Trace gases evolved from a polyimide film during its thermal curing stages have been studied using ion-induced nucleation mass spectrometry. The technique involved exposing the test gas sample to a low energy beta source and recording the masses of the ion-induced molecular clusters formed in the reaction chamber. On the basis of the experimentally observed molecular cluster spectra, it has been concluded that the dominant trace component had a molecular weight of 87 atomic mass units. This component has been identified as a molecule of dimethylacetamide (DMAC) which had been used as a solvent in the preparation of the test polyimide specimen. This identification has been further confirmed by comparing the spectra of the test gas sample and the DMAC calibration sample obtained with a conventional mass spectrometer. The advantages of the ion-induced nucleation mass spectrometer versus the conventional mass spectrometer are discussed.

INTRODUCTION

In recent years, the interest in atmospheric contaminants and pollutants as well as chemical agents has drawn considerable attention. The detection and analysis of trace compounds present in the atmosphere have become increasingly important. Ion-induced nucleation mass spectrometry techniques are now being investigated for the analysis of various trace contaminants,[1-7] and exhibit a broad applicability. The technique and application of ion-induced nucleation mass spectrometry is recognized as a potential analytical procedure for trace gas analysis.[8-12] Conventional ionization spectra using an electron impact ion source are difficult to utilize in trace gas analysis. Difficulties arise from the large number of fragment ions derived from each chemical constituent containing complex molecules. The development of ion-induced nucleation mass spectrometry has somewhat simplified the matter of trace compound analysis. This technique relies on the mass analysis of ions representing products of ion-molecule reactions taking place in the ion source region, operated in the pressure range from a fraction of a torr to 760 torr. The mass spectrum obtained in this manner can be expected to have prominent high mass peaks and will not contain fragment ion peaks that are predominant in a comparable electron impact mass spectrum. Potential applications of ion-induced nucleation mass spectrometry for trace gas analysis of several compounds have been reported for parts ratio in the range between 1 in 10^6 to 1 in 10^{14}.[13-14] The fundamental reason for this high sensitivity lies in selective clustering of the trace contaminant around ionic cores in the reaction chamber. This occurs by an extremely rapid preferential ionization process at relatively high

pressures. The primary ions for this study were produced by an 80 mCi ^{63}Ni beta ion source. These ions were produced at relatively high pressures (10.7 torr) as compared to the conventional electron impact ion source operating at 10^{-6} torr. The ionization efficiencies can be extremely high due to a preferential ionization process as shown in figure 1. This partly explains the potentially high sensitivities that can be obtained with this technique.

For this study, a sample of the test gas evolved during the thermal curing cycle of a polyimide film in a heated, forced-air oven was collected. This paper reports on an experimental study of positive ion clustering of trace molecular species in the test gas, with water molecules using ion-induced nucleation mass spectrometry techniques. The primary purpose of this study was to examine the possibilities of using ion-induced nucleation mass spectrometry techniques to determine the identity and concentration of molecular species evolved from a polyimide film during the thermal curing process.

Experimental Procedure

Apparatus.- Several important apparatus operational parameters are given in Table I. The mass spectrometer detection system is shown schematically in figure 2. This system has been described in some detail in references 11 and 12; therefore, only a brief description will be included here. Some changes were made for this study in order to reduce the possibility of contaminants. In previous studies[11-12] the reaction chamber was fabricated from a combination of 304 stainless steel and Pyrex glass using O-ring seals. In order to reduce the possibility of contaminants and atmospheric leaks from O-ring seals, it was necessary to replace the Pyrex glass section with 304 stainless steel. The reaction chamber in the present construction has all oxygen-free high conductivity (OFHC) copper gasket seals, with a total volume of approximately 2 liters.

A 5.1 cm (2 inch) diffusion pump system was added to the reaction chamber such that the reaction chamber could be baked at 300° C while maintaining a pressure in the range of 10^{-5} torr. Since the preselection ionization process is very sensitive, one must be very careful and pay scrupulous attention to cleanliness details. With the ability to bake the system at 300° C while maintaining a pressure in the reaction chamber of 10^{-5} torr the problem of cleanliness became manageable.

The test gas was introduced into the stainless steel reaction chamber from a 2 liter stainless steel gas canister through a variable leak metering valve. All of the test gas that enters into the mass spectrometer region must pass through the 80 mCi ^{63}Ni beta ion source where some of the test gas undergo a series of ion-molecule reaction.[8,15] Good et al., in reference 8, have shown that hydrate clusters of the type $H^+ \cdot (H_2O)_3$ and $H^+ \cdot (H_2O)_4$ become stationary after about 600 microseconds. The study in reference 8 was done with only water and nitrogen present. When other gases with a permanent dipole moment or gases with a significant polarizability are present in the reaction chamber the hydrates of water will interact strongly to form microclusters with a distribution of water molecules. The number and distribution of the water molecules that cluster with the trace molecules is strongly dependent on the local relative

humidity and the concentration levels of the trace molecules. From the ion source the ion microclusters are entrained with the neutral gas species and pass through a 25-micron diameter stainless steel sampling aperture into the mass spectrometer region where the pressure was maintained in the range of 3×10^{-6} torr. The mass spectrometer region was maintained at a low pressure using a large liquid nitrogen cold trap and a 15 cm (6 inch) diffusion pump system. The effective pumping speed of this system was several hundred liters per second. In order to provide a reference for reproducible results, the relative humidity was maintained at a constant level by bubbling the carrier gas (laboratory grade nitrogen) through distilled water. The addition of extra water molecules to the test gas is not expected to affect the conclusions regarding the identity of other molecular species evolved from the test specimen.

The 25-micron diameter sampling aperture was maintained at a positive 15 volts with respect to ground and gave the positive ions initial momentum in the direction of the focussing lens system at the front of the quadrupole mass spectrometer. All potentials on the lens elements were precisely controlled to maintain a constant electrical potential for focussing purposes. For calibration purposes the internal lens system at the entrance to the mass spectrometer was designed with a filament as a conventional electron bombardment ion source for routine calibrations. Positive ion spectra for calibration were obtained using the electron impact ion source spectrum of nitrogen, carbon dioxide, sulfur hexafluoride (SF_6), and perfluorotributlyamine (FC-43).[16-17] These gases give identification peaks in the low, medium, and high mass range. The quadrupole mass spectrometer used in this study had a mass resolution, $M/\Delta M$, of 600 at mass 600. The ionic microclusters obtained from the reactions of trace organic molecules and water are not expected to have a ΔM of less than 2 amu. Therefore, it would appear that the instrument has adequate resolution for this study.

Signal detection procedure.- From the ^{63}Ni beta source region positive ions are entrained with the carrier gas from the reaction chamber through the 25-micron diameter stainless steel collimating pinhole aperture. The microcluster ions follow their expansion trajectories until they are close enough to be controlled by the ion lens system. After passing through the quadrupole mass analyzer, the ions were detected with a 14-stage Be-Cu electron multiplier and a picoammeter. The observed microcluster spectrum was obtained using a strip chart recorder connected to the output of the picoammeter. Typically, the electron multiplier gain was on the order of 5×10^5.

RESULTS AND DISCUSSION

A typical microcluster spectrum is shown in figure 3 for a reaction chamber pressure of 10.7 torr. For this spectrum the mass spectrometer was set for a scan rate of approximately one atomic mass unit (amu) per second. In figure 3, there is clear evidence of water hydrates clustering with trace species having a molecular weight of 87 amu. For this study, the material used in the preparation of the polyimide film is shown in figure 4. It is evident from this figure that one of the major components of the polyimide film is dimethylacetamide (DMAC) solvent. The DMAC molecule has a molecular weight of 87 amu, this strongly

suggests that the trace specie in the test gas sample was a DMAC molecule. The number (n) of DMAC molecules in the microcluster range from 0 to 5 while the number (m) of water molecules range from 1-26. Results by other investigators on other systems[9,10] have shown that the number of water molecules in micro-cluster studies of the type $(H_2O)_m.H^+$ can range from 1 to a large number. The primary ionization products in the ^{63}Ni beta source region were N_2^+, the ions of the trace compounds of H_2O and DMAC, and electrons. However, given suffi-cient time to react, the terminal positive ions would almost entirely be of the form $(H_2O)_m.H^+$. The dominant $(H_2O)_m.H^+$ ions are believed to be the catalyst for the formation of essentially all the $(DMAC)_n.(H_2O)_m.H^+$ microclusters in the source region as shown in figure 1. The mass spectrometer used in this study had a mass range of approximately 800 amu. Therefore, if microclusters were formed with higher mass numbers, they would not have been detected.

In order to get a measured standard of the concentration levels of DMAC collected from the forced air oven during the curing stages of the polyimide films, a test procedure was initiated. A silica gel absorption tube was used to pump 50 ml of forced-air from the test oven. An analysis of the silica gel absorption tube was analyzed for DMAC concentration. The analysis was performed in accordance with NIOSH procedures, method No. 5254; with one exception. The chromatograph column employed was changed to a 610 cm (20') x 0.32 (.125") 10% FFAP on chromasorb W-AW rather than the column recommended in the procedure. This change was made as a matter of convenience and availability and is not expected to influence the result. The sample was desorbed in 1.0 ml of methanol for 1 hour. In addition, the sample was placed in an ultrasonic bath to aid desorption. DMAC standards were prepared in 1.0 ml of methanol and were analyzed prior to the sample. The analysis was performed on a Hewlett Packard 5880 Gas Chromatograph equipped with a flame ionization detector. A plot of peak area versus standard concentration enabled the determination of DMAC concentration of the sample. This analysis yielded concentration levels of DMAC in the PPM ranges desorbed from the silica gel tube.

Figure 5 shows the conventional spectrum of the test gas. In this figure, there is evidence of mass 87 appearing in the spectrum. The mass 87 peak could not be seen using conventional mass spectrometry until the air background was subtracted. This spectrum also shows how hot filament ion sources cause fractionation of chemical bonds in complex molecules. The mass peaks occurring at 15, 42, 43, 44, 45 amu and others are due to fractionation of the DMAC molecules. Although the two spectra in figures 3 and 5 were taken from the same test gas sample, they appear to be quite different. This is due to the differ-ence in the ionization mechanism of the ^{63}Ni ion source and the hot filament ion source. For complex molecules, the task of trying to analyze a conventional mass spectrum could be very difficult. In comparing the data from the hot filament and ^{63}Ni ion source, it is apparent that the hot filament source would be best for studying lighter molecules or trace molecules with well-known fragmentation patterns. However, for trace gas analysis the ^{63}Ni ion source offers greater simplicity and versatility since the parent molecules appear in the mass spec-trum unfragmented.

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CONCLUDING REMARKS

The results of this work have shown that PPM concentrations of solvents such as DMAC lost from polyimide films during the curing stages can be detected using microcluster ion-induced nucleation mass spectrometry. The mass spectrum obtained using a ^{63}Ni source is relatively simple; microclusters are formed by successive additions of DMAC molecules to water hydrates. Improvements in the ability to detect smaller concentrations can be obtained by using multiplier with gains on the order of 10^8. Also, pulse counting techniques can improve the signal-to-noise ratio in the detection system. In summary, this implies that concentration levels of 1 part in 10^{11} detectability for several trace gas components. The implications of these results are significant for detecting low level concentrations of molecular species evolved from polyimide films during the curing stages. High-pressure, ion-induced nucleation mass spectrometry is a technique used for studying the chemical nature of complex molecular species. Under well-controlled conditions it can also provide quantitative information about the total mass of the evolved species as pointed out by Singh et al.[11,12]
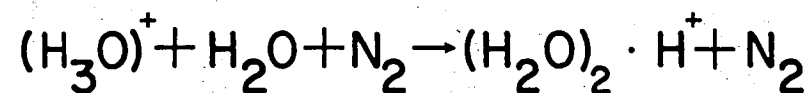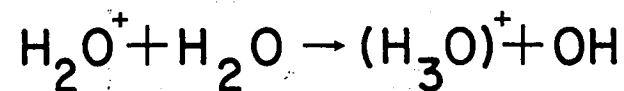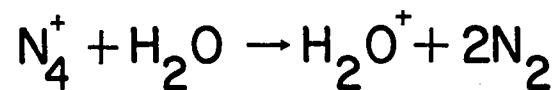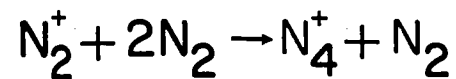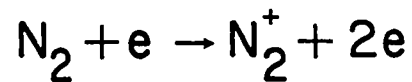
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TABLE I – EXPERIMENTAL PARAMETERS

REACTION CHAMBER PRESSURE	10.7 torr
REACTION CHAMBER TEMPERATURE	28.6 °C
RELATIVE HUMIDITY IN REACTION CHAMBER	1.9 %
DEWPOINT TEMPERATURE IN REACTION CHAMBER	-26.1 °C
MASS SPECTROMETER PRESSURE	3×10^{-6} torr
CARRIER GAS FLOW RATE (N_2)	30 ml/min

$$N_2 + e \rightarrow N_2^+ + 2e$$

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$$

$$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2$$

$$H_2O^+ + H_2O \rightarrow (H_3O)^+ + OH$$

$$(H_3O)^+ + H_2O + N_2 \rightarrow (H_2O)_2 \cdot H^+ + N_2$$

$$\vdots$$

$$(H_2O)_m \cdot H^+ + x \left(\begin{smallmatrix} \text{TRACE} \\ \text{MOLECULE} \end{smallmatrix} \right) \rightarrow \left(\begin{smallmatrix} \text{TRACE} \\ \text{MOLECULE} \end{smallmatrix} \right)_n \cdot (H_2O)_{m'} \cdot H^+$$

$$+ \left(\begin{smallmatrix} \text{TRACE} \\ \text{MOLECULE} \end{smallmatrix} \right)_{x-n} + (H_2O)_{m-m'} \ (m' \leq m)$$
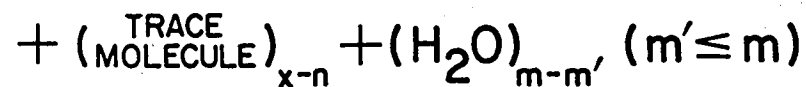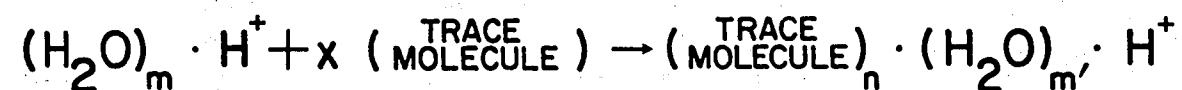
FIGURE 1 - FORMATION OF $\left(\begin{smallmatrix} \text{TRACE} \\ \text{MOLECULE} \end{smallmatrix} \right)_n \cdot (H_2O)_{m'} \cdot H^+$
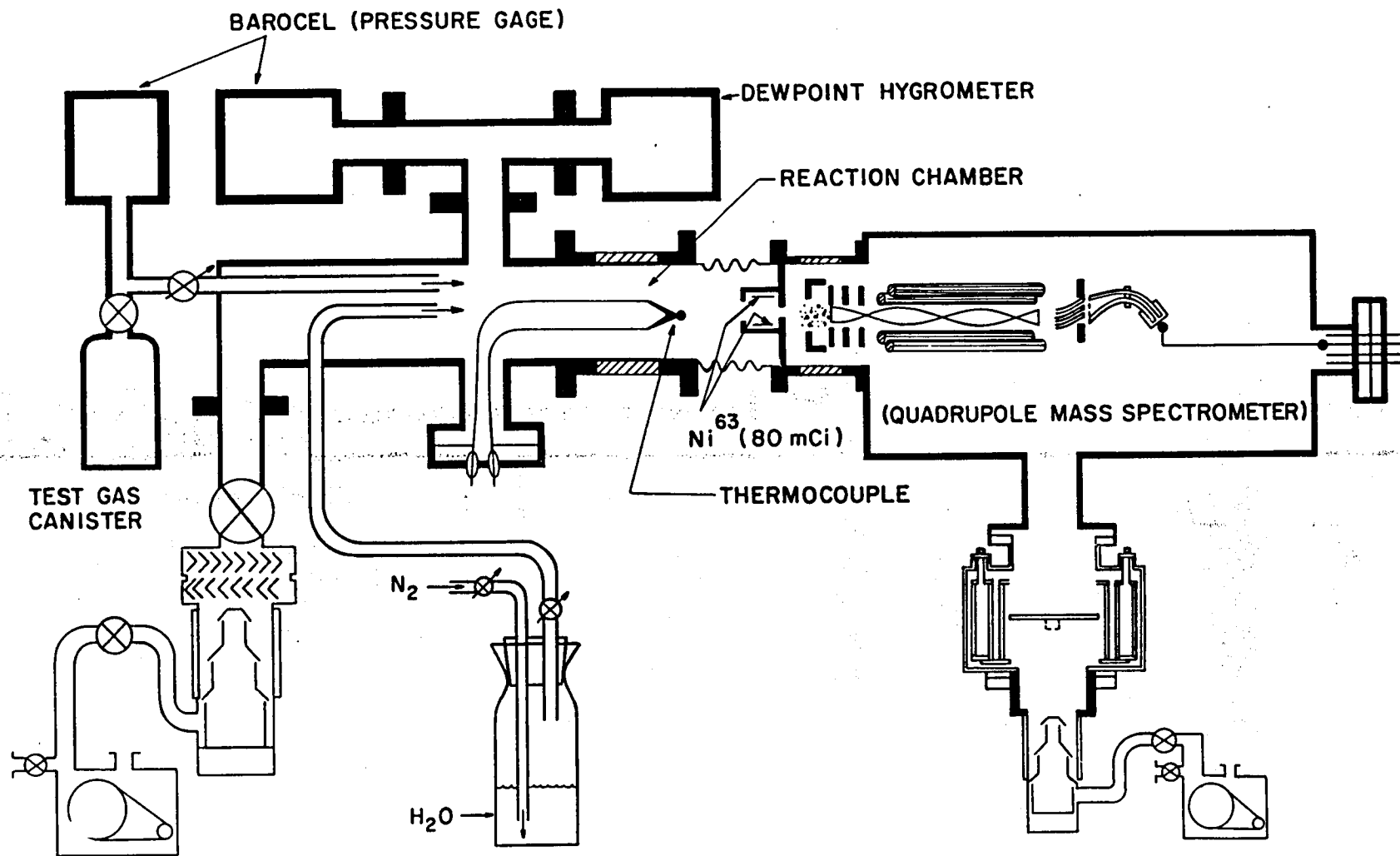
MICROCLUSTERS

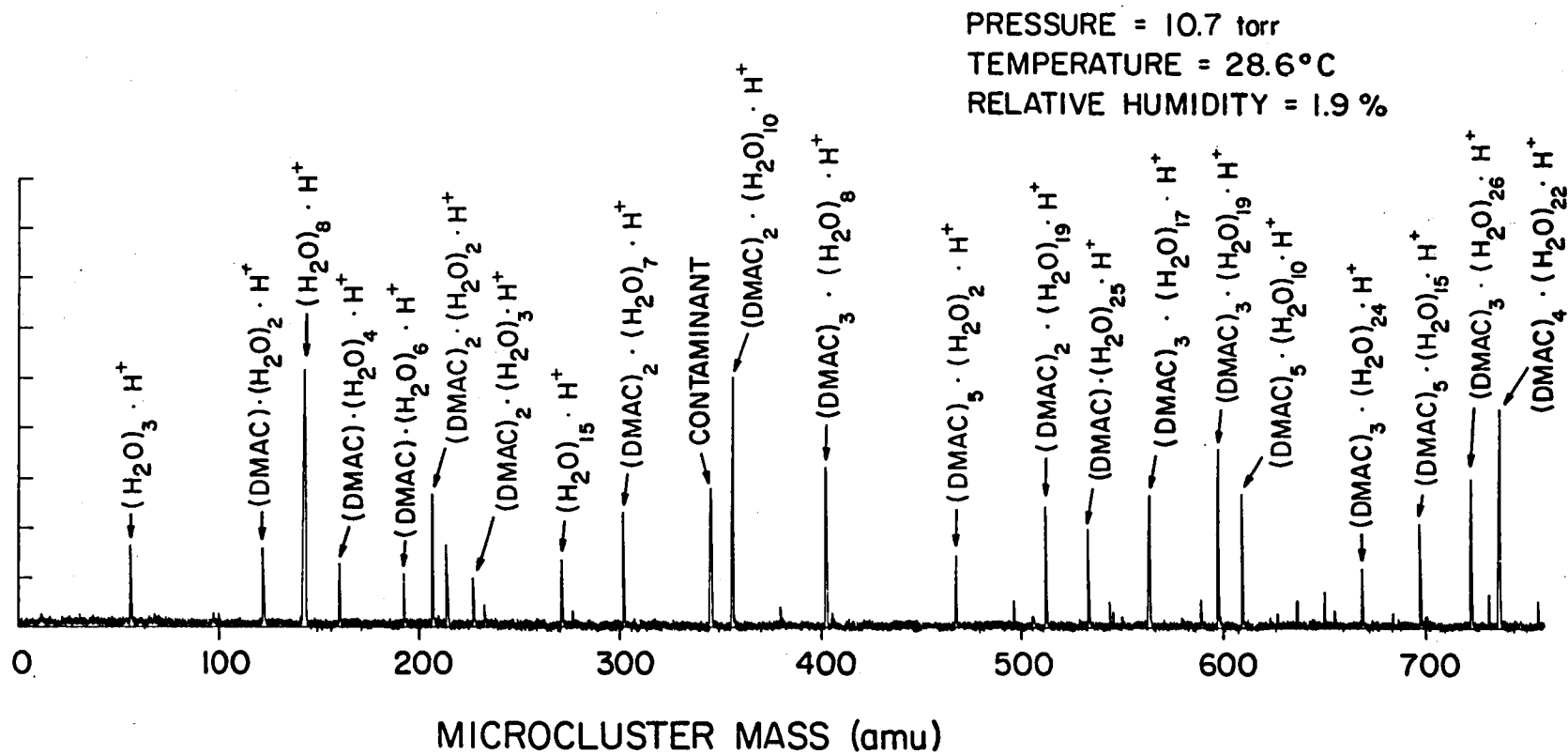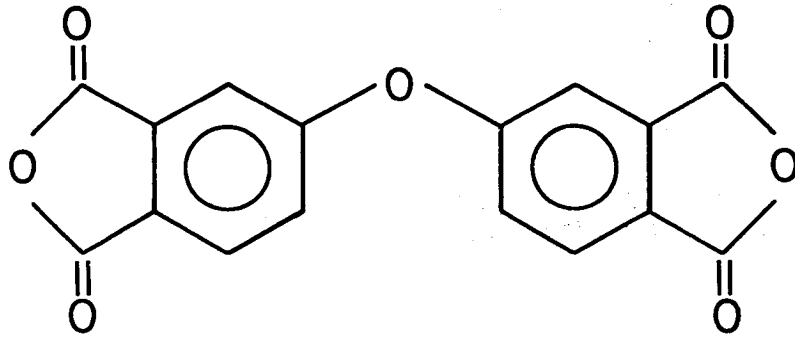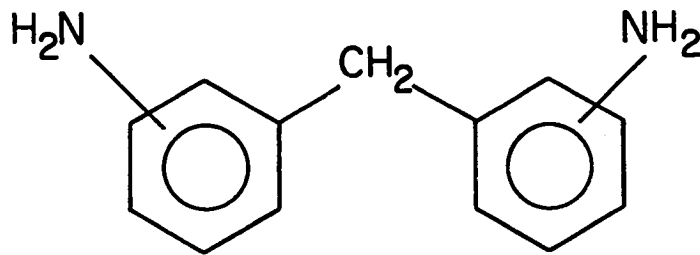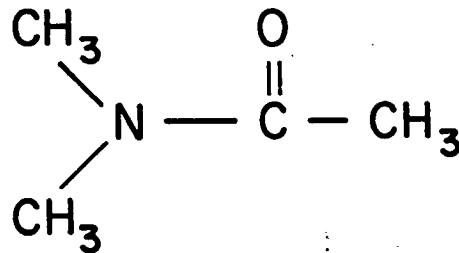FIGURE 2 - SCHEMATIC DIAGRAM OF THE MICROCLUSTER SPECTROMETER SYSTEM

FIGURE 3 - TYPICAL MICROCLUSTER MASS SPECTRUM

OXYDIPHTHALIC ANHYDRIDE (ODPA)

METHYLENEDIANALINE (MDA)

DIMETHYLACETAMIDE (DMAC)
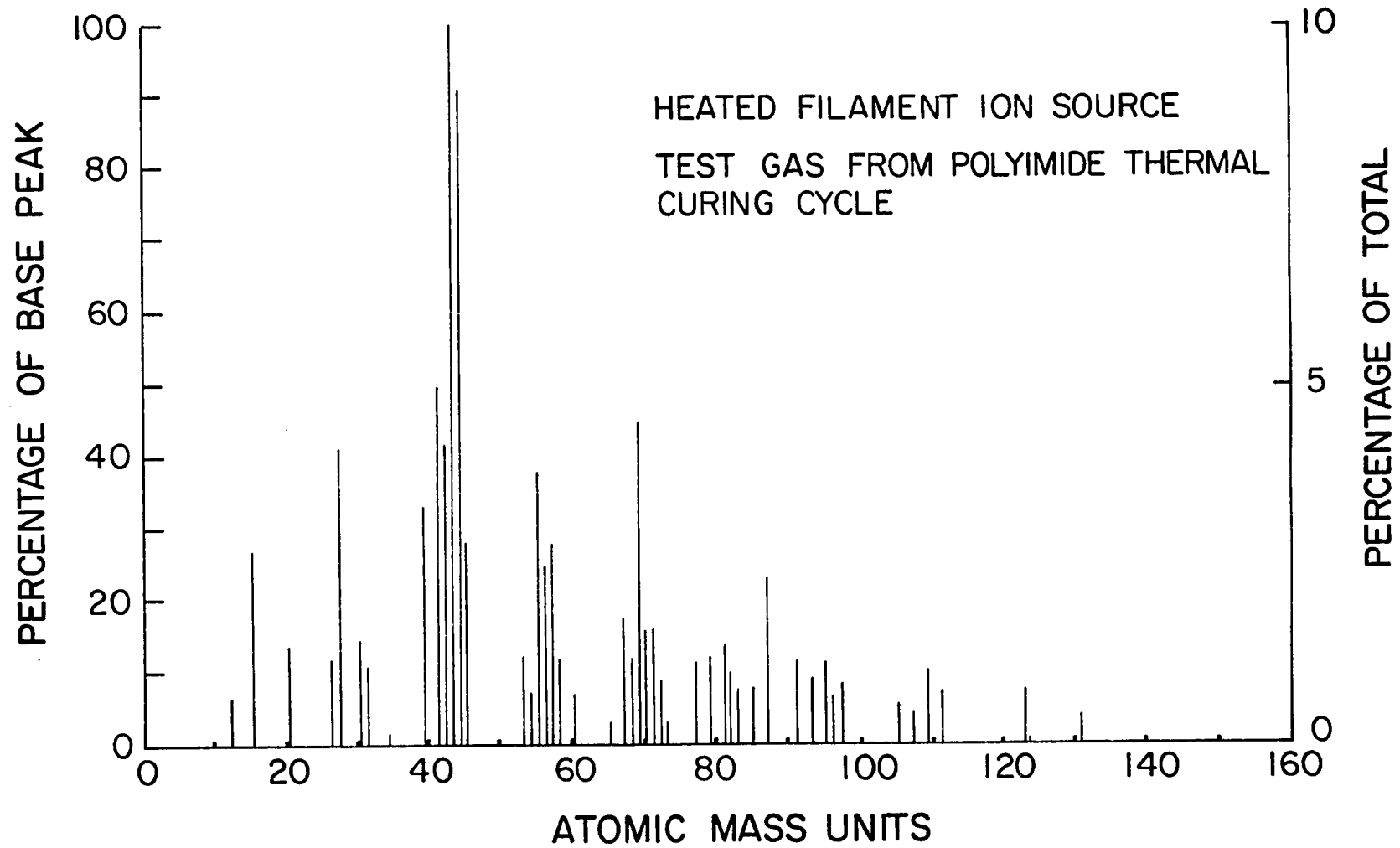
FIGURE 4 – MATERIALS USED FOR MAKING
POLYIMIDE FILMS.

FIGURE 5 - MASS SPECTRUM OF THE TEST GAS (AIR BACKGROUND SUBTRACTED)

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		14. Army Project No.

15. Supplementary Notes

16. Abstract

    Trace gases evolved from a polyimide film during its thermal curing stages have been studied using ion-induced nucleation mass spectrometry. The technique involved exposing the test gas sample to a low energy beta source and recording the masses of the ion-induced molecular clusters formed in the reaction chamber. On the basis of the experimentally observed molecular cluster spectra, it has been concluded that the dominant trace component had a molecular weight of 87 atomic mass units. This component has been identified as a molecule of dimethylacetamide (DMAC) which had been used as a solvent in the preparation of the test polyimide specimen. This identification has been further confirmed by comparing the spectra of the test gas sample and the DMAC calibration sample obtained with a conventional mass spectrometer. The advantages of the ion-induced nucleation mass spectrometer versus the conventional mass spectrometer are discussed.

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