JOURNAL OF MASS SPECTROMETRY, VOL. 31, 464–471 (1996)

Analysis of Gaseous Ammonia, Volatile Primary Amines and Quaternary Ammonium Salts at Subambient Temperature by Liquid Secondary Ion Mass Spectrometry

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Low-temperature matrix systems were developed for effectively obtaining liquid secondary ion mass spectrometric (LSIMS) signals from gaseous ammonia and volatile primary amines. A good LSI mass spectrum of ammonia gas was obtained by absorbing the gaseous ammonia molecule on the surface of the liquid nitrogen-frozen glycerol matrix. For the analysis of volatile primary amines, the sample is first dissolved in methanol and a small amount of the solution is then applied directly on the glycerol matrix, which has been frozen with liquid nitrogen beforehand. Since the surface of the frozen glycerol matrix melts on contact with the methanol solution, the viscosity of the matrix in this region is suitable for LSIMS analysis. However, as the temperature in the bottom part of the matrix is still low, this will reduce the volatility of the analyte molecules and retain them on the matrix surface. The mass spectra recorded under these conditions are of good quality and show strong analyte signals. This technique has also been demonstrated to be very useful in eliminating the surface activity effect among series of quaternary amines on their LSI mass spectra.

KEYWORDS: liquid secondary ion mass spectrometry; subambient temperature; diglycerol; volatile organic compounds

INTRODUCTION

Temperature effects in liquid secondary ion mass spectrometry (LSIMS) or fast atom bombardment mass spectrometry (FAB) have seldom been investigated. In the last 10 years, only a few groups of workers have made such studies, and the objective of these studies was to elucidate the mechanisms of desorption and ionization.[1–8] For example, the FAB or secondary ion mass spectra of small molecules such as nitrogen,[1] water,[2] acetone[3] and methanol[4] have been obtained in the solid state at temperatures ranging from 15 to 77 K and the mass spectra of common LSIMS/FAB matrices, glycerol and polyethylene glycol, have also been reported at temperatures below $-20\,^{\circ}C$.[5] However, virtually no studies have been made of the application of LSIMS to the analysis of gaseous or volatile organic compounds at low temperature. The development of such techniques may be very useful for rapidly detecting and identifying volatile organic components in samples.

Although the matrix together with volatile analyte can easily be frozen and then subjected to LSIMS/FAB analysis, it has been reported that the degree of degradation of the mass spectra increases as the matrix temperature decreases.[5] At very low temperatures, a heavily degraded mass spectrum will usually be obtained. The spectrum is characterized by extensive fragment ions and chemical noise and no analyte signal can be seen.[5,7,8] Sunner *et al.*[9] have pointed out that the influence of the temperature change on the ion–molecule reactions is small. Subsequently, Shiea and Sunner[8] reported that the high viscosity of the glycerol matrix at low temperatures may be responsible for the degradation of the FAB mass spectra. They suggested when the temperature of the matrix is low (or the viscosity is high), a high-temperature gas will be developed at the bottom of the bombarding cavity. This will result in the gas taking a longer time to expand into the vacuum. As the collision cascade energy becomes equi-partitioned among the different degrees of freedom, the intermolecular collisions become more violent and 'pressure' builds up. If the 'walls' of the cavity are rigid (high viscosity at low temperature), this pressure will be released upwards, imparting a momentum to the gas and rapid expulsion of all the 'hot' gas is ensured. The expected result is spectra that are dominated by chemical noise and fragment ions.

Owing to their even higher volatility in vacuum, the LSIMS analysis of volatile organic compound usually

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CCC 1076–5174/96/050464–08

Received 11 July 1995
Accepted 22 December 1995

cannot be performed unless strongly non-volatile acids such as polyphosphoric acid and sulphuric acid are used as the matrices.[10,11] The signal from non-volatile analyte ions was also enhanced by adding non-volatile acids such as sulphuric and *p*-toluenesulphonic acid to the glycerol matrix.[12,13] However, only chemicals which are stable (e.g. trialkyl phosphonates and aromatics with deactivating substituents) in the acidic solution can be analysed by both approaches. Signals of volatile amines have also been reported to be obtained by adding concentrated HCl to the matrix,[12] because a non-volatile amine–HCl salt was formed. Again, the technique is limited to chemicals which are stable in the acidic environment.

The other strategy to obtain a signal from volatile organic compounds by LSIMS is to run the analyte–matrix at subambient temperature. Since volatility decreases with decrease in temperature, the analyte molecules will be retained in the matrix in the LSIMS source. However, the viscosity of the matrix cannot be too high or good mass spectra cannot be obtained. In this work, low-temperature LSIMS/FAB matrix systems were developed and good mass spectra of gaseous ammonia and volatile primary amines were obtained. In much the same way, the matrix system was also used to analyse a series of quaternary amines with different alkyl chain lengths. It was found that the surface activity effect among the sample molecules can be successfully eliminated.

EXPERIMENTAL

All chemicals were obtained from Sigma or Aldrich and used without further purification. To create low-temperature conditions for the analysis of primary amines and quaternary ammonia salts, the matrix (1.5 μl of glycerol or diglycerol) was applied on the probe tip, which was then immersed in a liquid nitrogen bath for 3 min. To prevent moisture from forming a coating on the cold probe, the surface of the probe was wrapped with aluminium foil before cooling. After removing the foil, 0.5 μl of sample solution (in methanol) was applied directly on the surface of the frozen matrix. The probe was then rapidly inserted in the LSIMS source for analysis. The probe temperature relaxed towards 25 °C with a half-life of about 5 min.

For the analysis of gaseous ammonia, the probe tip together with the glycerol matrix was immersed in the liquid nitrogen bath for 5 min. The probe was then set 2 cm above a bottle containing ammonia solution for 30 s. The probe was then inserted in the LSIMS source for analysis.

The LSI mass spectra were obtained on a VG Quattro mass spectrometer equipped with a direct insertion probe and a caesium ion gun. The discharge current of the caesium ion gun was operated at 1 mA with a voltage of 10 kV. The mass resolution was set around 1000. The mass spectrometer was scanned from *m/z* 1000 down to 10 in 5 s and the inter-scan delay time was 0.5 s. For each sample, triplicate LSIMS analyses were performed. The mass spectra from the first three scans were averaged and are reported here.

RESULTS AND DISCUSSION

Analysis of volatile primary amines and gaseous ammonia at subambient temperature

Figure 1(a) shows the LSI mass spectrum of isopropylamine (0.005 M in methanol). The sample solution was directly applied on the surface of the glycerol matrix at room temperature. The signal from isopropylamine (MH^+, *m/z* 60) is not observed on the spectrum. Owing to very high volatility of isopropylamine (b.p. 33 °C), it is impossible to keep the analyte mol-

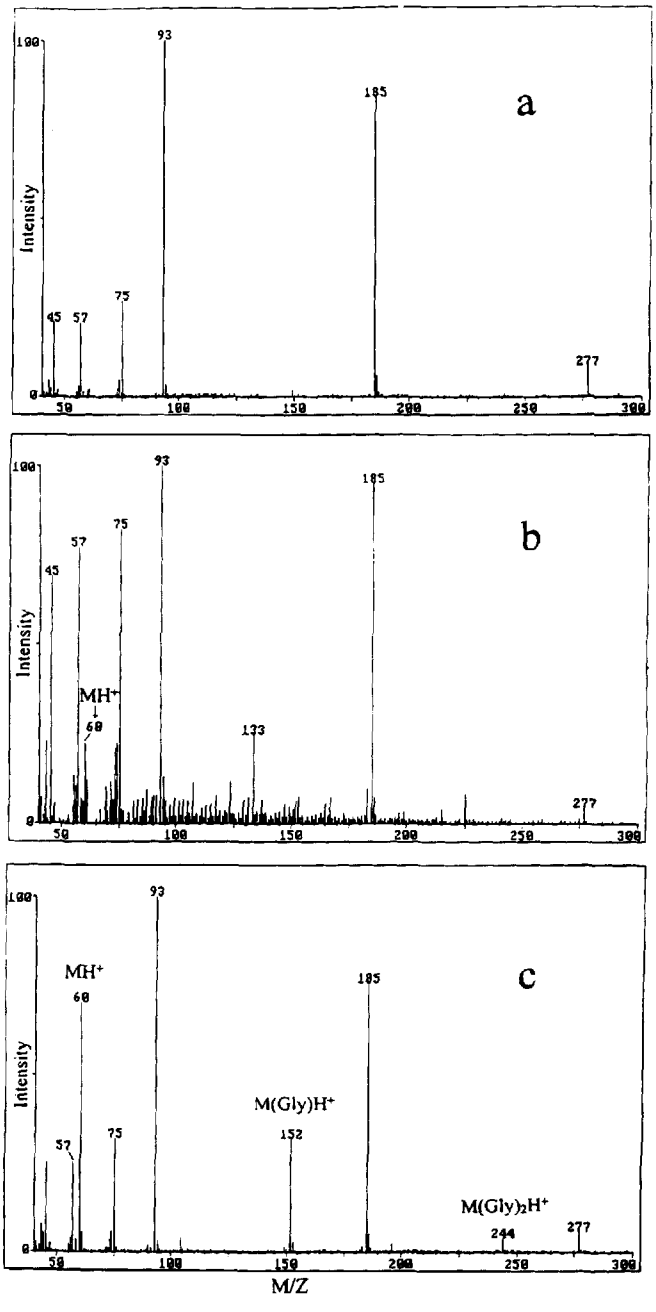

Figure 1. Positive LSI mass spectra of a sample solution containing 0.005 M isopropylamine in methanol. The sample solution was applied directly on the surface of (a) a glycerol matrix at room temperature and (c) a liquid nitrogen-frozen glycerol matrix. The spectrum in (b) was obtained by directly dissolving the analyte in glycerol and then freezing the smple solution with liquid nitrogen.

ecules in the matrix in the LSIMS source, particularly when a very low pressure was maintained in the source. Decreasing the matrix temperature and the volatility of the analyte by freezing the sample solution (analyte dissolved in glycerol) with liquid nitrogen was not very helpful in obtaining good LSI mass spectra [Fig. 1(b)], because the viscosity of the glycerol also increases as the temperature decreases. Figure 1(c) shows the LSI mass spectrum which was obtained by directly applying the analyte solution (in methanol) on the surface of the liquid nitrogen-frozen glycerol matrix. Under these conditions, a very strong signal from protonated isopropylamine is seen on the spectrum. Since the temperature of the methanol solution is about 22 °C, once it has been applied on the frozen glycerol matrix, it is expected that the surface of the matrix will melt. The viscosity in this region is then suitable for LSIMS analysis. However, since the temperature in the bottom part of the matrix (and also the probe tip) is still low, the volatile sample molecules will be retained on the surface of the matrix. Good, strong signals from the analyte were seen on the mass spectrum.

With the same strategy, a good LSI mass spectrum of gaseous ammonia can be obtained [Fig. 2(b)]. The gaseous ammonia molecules were absorbed on the surface of liquid nitrogen-frozen glycerol matrix on the probe tip. This was done by simply setting the liquid nitrogen-frozen glycerol matrix (on the probe tip) just above the orifice of a bottle containing ammonia solution for 30 s. The distance between the frozen glycerol matrix and the ammonia solution was 5 cm. The probe was then inserted in LSIMS source for analysis. The interaction between gaseous ammonia and frozen glycerol molecules is so strong even at low pressure, such as in the LSIMS source, that the ammonia molecules are still retained on the surface of the matrix. The viscosity of the matrix is high under these conditions but, owing to its small size and strong N—H bond, a very strong signal from the ammonium ion (NH_4^+, m/z 18) can be seen [Fig. 2(b)]. Other than the NH_4^+ ion, a strong signal from the (glycerol)NH_4^+ adduct ion (m/z 110) can also be seen. Figure 2(a) shows the LSI mass spectrum obtained in the same way except that the ammonia molecule was absorbed on the glycerol matrix

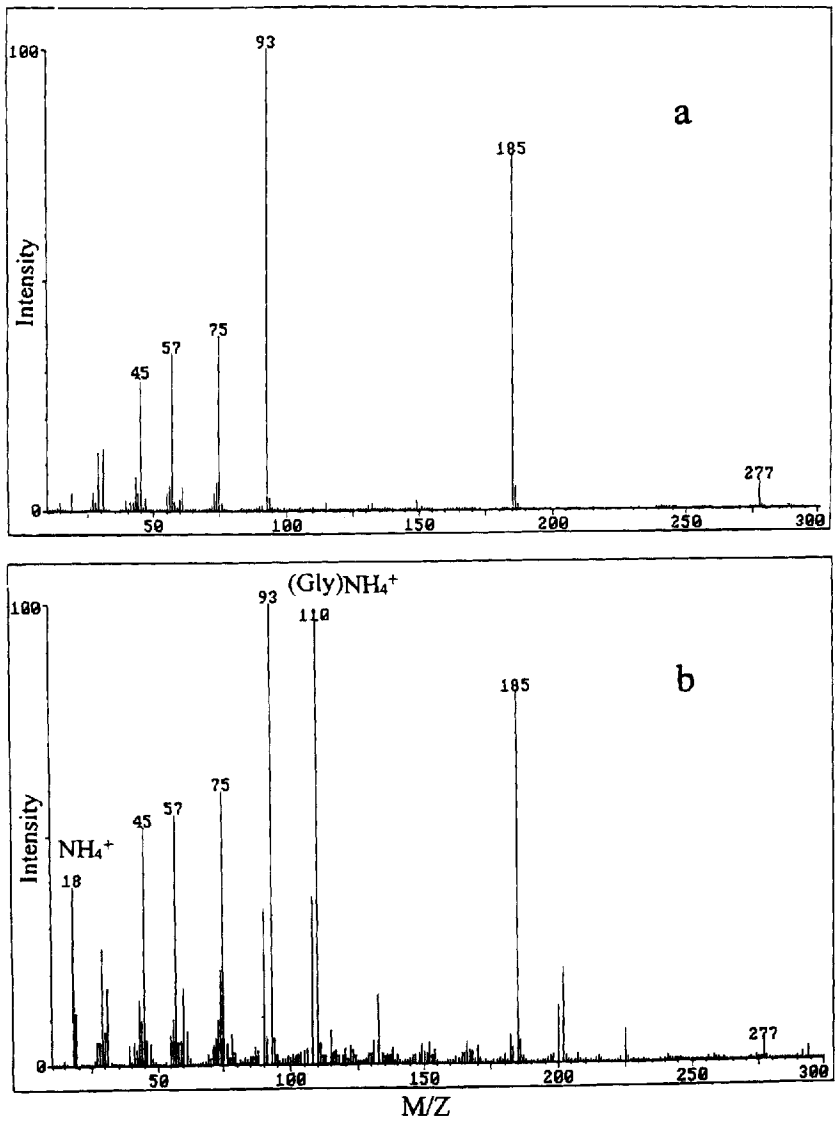

Figure 2. Positive LSI mass spectra of gaseous ammonia absorbed on the surface of (a) a glycerol matrix at room temperature and (b) a liquid nitrogen-frozen glycerol matrix.

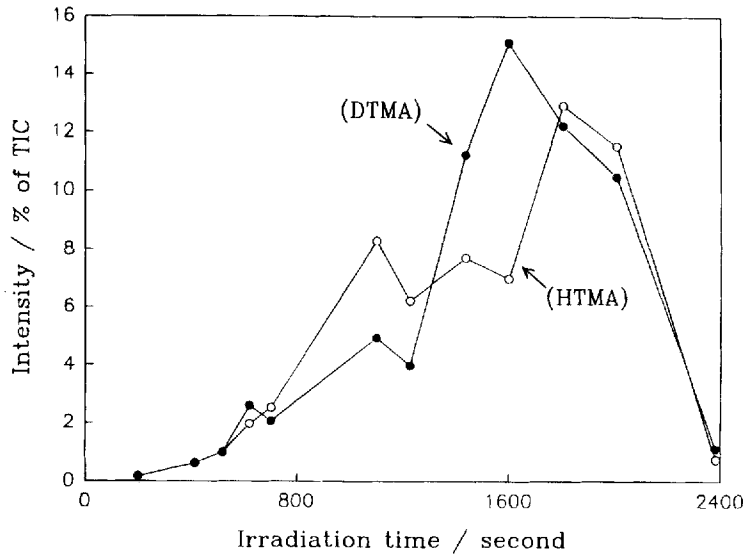

Figure 3. Change in percentage of total ion current (% of TIC) of intensities of dodecyltrimethylammonium bromide (DTMA) and hexadecyltrimethylammonium bromide (HTMA) with respect to the irradiation time in LSIMS. Both analytes were dissolved in glycerol at equal concentrations (0.002 M) and the solution was then cooled by immersing the probe together with the sample solution in a dry-ice bath for 2 min before insertion in the LSIMS source.

at room temperature. No signal from ammonia can be seen on the mass spectrum.

Relative response of ion signal of quaternary and primary amines with different surface activities at subambient temperature

It has been shown that for a series of analytes the intensities of the LSIMS or FAB signals were determined by their relative surface concentration on the matrix.[14] This observation is particularly important for LSIMS, since it has been recognized that the composition of the top few layers of liquid solutions may differ from the bulk composition.[15] Also, it has been suggested that during LSIMS, the sample molecules can be brought up to the matrix surface by fast mass transport processes such as diffusion, charge migration and convection.[16,17] The same processes may also be involved in bringing the sample molecules from the surface down to the matrix. Nevertheless, the relative importance of these processes is still unclear. Ligon and Dorn[18] have shown that for a series of surfactants, the differences in ion sensitivities on the mass spectra are due almost exclusively to their surface activity. This is because the surface sites of the matrix tend to be occupied by the more surface-active analytes, and the molecules on this surface will then be ionized by FAB. Therefore, to determine accurately the quantity of organic species by LSIMS it is necessary to understand how the surface composition differs from the bulk composition, since it is the surface composition of the matrix that will be reflected in the mass spectra.

Applying the sample solution (in a volatile solvent) directly on the surface of the matrix (at room temperature) has been found useful for increasing the surface concentration of certain analytes (e.g. porphyrins) and their signals on the mass spectrum.[19] However, in most other cases this precipitation technique is not very helpful. This is because rapid downward diffusion, migration or convection of the analyte molecules in the matrix may occur when the solution is introduced into the ion source.[20,21] The driving forces for these actions may come from sudden evaporation of the matrix molecules in the vacuum, ascension of the gas bubbles in the matrix or changes in surface composition by the impact of the primary ions.[22] Therefore, the concentration of the analyte molecules on the surface was not as great as expected.

However, if the sample solution was applied on the surface of the matrix and all mass transport processes were blocked prior to the impact by the primary ions, ideally, the analyte molecules should remain on the surface and no surface activity effect on the mass spectra should be seen. A simple way to achieve this goal is to increase the viscosity of the matrix to inhibit the occurrence of mass transport processes in it. Nevertheless, the viscosity of the matrix in the bombarding area cannot be too high, otherwise the spectra may decay. In a previous paper,[8] we showed that the transport process of the analyte in the matrix is strongly viscosity (and temperature) dependent. Since the viscosity of glycerol increasing rapidly with decrease in temperature, lowering the temperature of the matrix should be an efficient way to slow down the movement of the analyte molecules in the matrix.[8,23]

To study the relationship between ion abundance and matrix viscosity at low temperatures, two quaternary ammonium bromides, n-$C_{12}H_{25}N(CH_3)_3Br$ (DTMA) and n-$C_{16}H_{33}N(CH_3)_3Br$ (HTMA), were chosen as analytes. Both are precharged in the solution and have similar structures except for the surface activity.

The sample solution was prepared by dissolving equal concentrations of the analytes in glycerol. After applying the solution on the probe tip and cooling in a dry-ice bath for 5 min, the sample was rapidly inserted in the LSIMS source for analysis. The temperature of the solution was $-45\,^{\circ}C$ (measured with a thermistor).

Figure 3 shows the change in the percentage of total ion current (% of TIC) of DTMA and HTMA as a

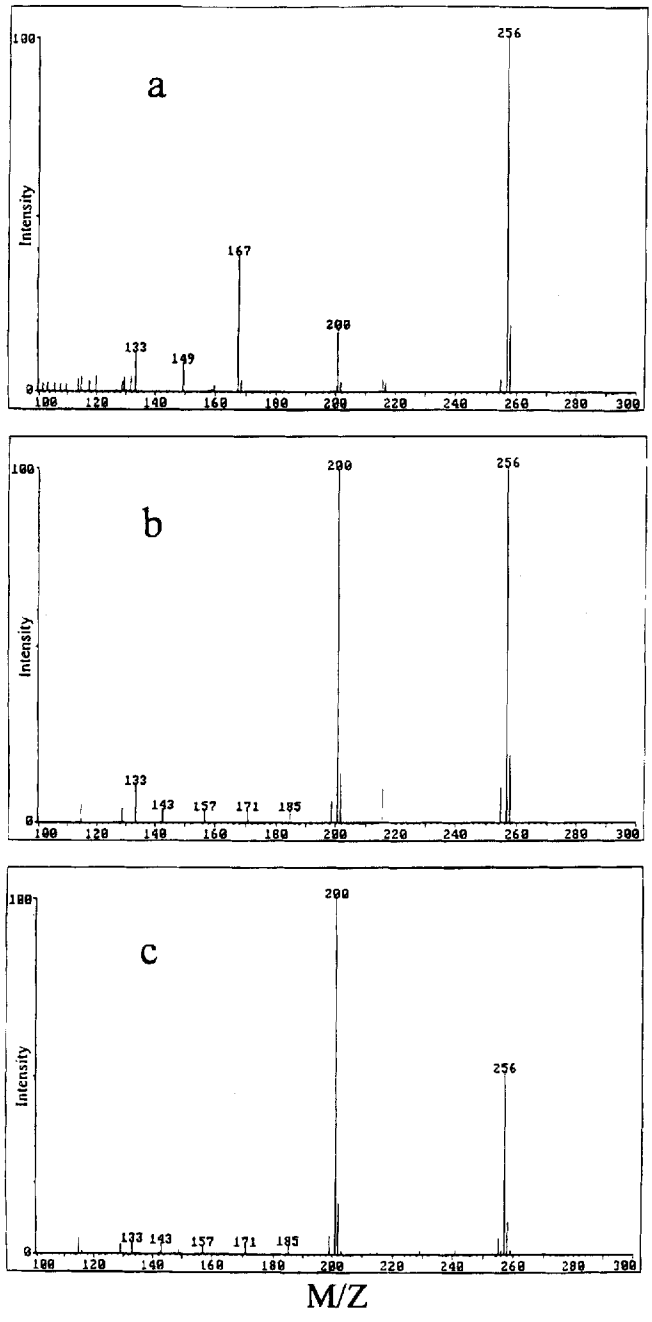

Figure 4. Positive LSI mass spectra of a sample solution containing 0.001 M decyltrimethylammonium bromide (DTMA, *m/z* 200) and tetradecyltrimethylammonium (TTMA, *m/z* 256). The sample was dissolved in methanol and then applied on the surface of (a) a diglycerol matrix at room temperature, (b) a liquid nitrogen-frozen diglycerol matrix and (c) the same as in (b) except that the concentration of DTMA was 0.002 M and that of TTMA was 0.001 M.

function of irradiation time in the ion source. Under such low-temperature conditions, the signal from both analytes is low, however, it is interesting to see that the trends of the changes in % of TIC of DTMA and HTMA with irradiation time in the LSIMS source are similar. It is important to note that there were variations in the spectra between different experiments run on different occasions. However, the trends in the data were always similar. The results indicate that when the viscosity of the matrix is high, the mass transport processes of the analyte molecules seems to be blocked and the mass spectra reflect the true concentration of the analytes in bulk solution. In this case, the effect of difference in surface activity of the analytes is removed.

These results imply that for a series of analytes a quantitative LSIMS analysis might be performed when the mass transport processes are blocked under low-temperature conditions. The problem that remains is how to keep the temperature low enough but still obtain good LSI mass spectra. It seems that the strategy used in the analysis of isopropylamine can also be used here.

Figure 4 shows the LSI spectra obtained from a methanol solution containing equal concentration of DTMA and TTMA applied on the surface of (a) diglycerol and (b) liquid nitrogen-frozen diglycerol matrices. Since the viscosity of diglycerol is higher than that of glycerol, the rate of mass transport processes in diglycerol will be much slower and more of the analyte molecules may remain on the matrix surface. The gas-phase basicity of diglycerol is not known, but, we expect it to be very similar to that of glycerol owing to their structural similarity. Therefore, diglycerol instead of glycerol was chosen as the matrix in this study. It can be seen that when the matrix was kept at room temperature, even though the sample solution was applied directly on the surface of the matrix the signal of TTMA was still much higher than that of DTMA [Fig. 4(a)]. As discussed previously, fast downward mass transport processes may occur on sample application and at the moment when the probe is inserted into the vacuum chamber. The surface of the matrix is then occupied by more surface-active molecules (i.e. TTMA) and the LSI mass spectrum reflects the difference in their surface activities.

When the matrix was frozen in liquid nitrogen before the application of sample solution, the respective molecular ions of both analytes showed nearly equal responses [Fig. 4(b)]. The result reflects the true condition of the bulk solution, i.e. equal concentrations of both analytes were present in the solution. The intensity of signal of the analyte is also enhanced. This is because owing to the low temperature and high viscosity in the bottom part of the matrix, all of the analyte molecules are forced to remain on the matrix surface, thereby increasing their surface concentration and the LSIMS signal. The responses of the LSIMS signals from both analytes are nearly equal for a period of time and then separate when the matrix has completely dissolved. The length of time depends on how well the probe and the matrix are cooled and it can last from 3 to 10 min. When the concentration of DTMA in the bulk solution doubles, its LSIMS signal response is also doubled [Fig. 4(c)].

Figure 5 shows the LSI mass spectra of a sample solution which contains equal concentrations of C_8-, C_{10}-, C_{12}-, C_{14}- and C_{16}-alkyl trimethyl quaternary amines in the bulk solution (the subscripts refer to the carbon numbers in the alkyl chain). The diglycerol matrix was kept at room temperature [Fig. 5(a)] or frozen by liquid nitrogen [Fig. 5(b)]. It can be seen that the difference in signal intensities among the quaternary amines is much smaller when liquid nitrogen-frozen diglycerol was used. Again, there were variations in the spectra between different experimental runs. However,

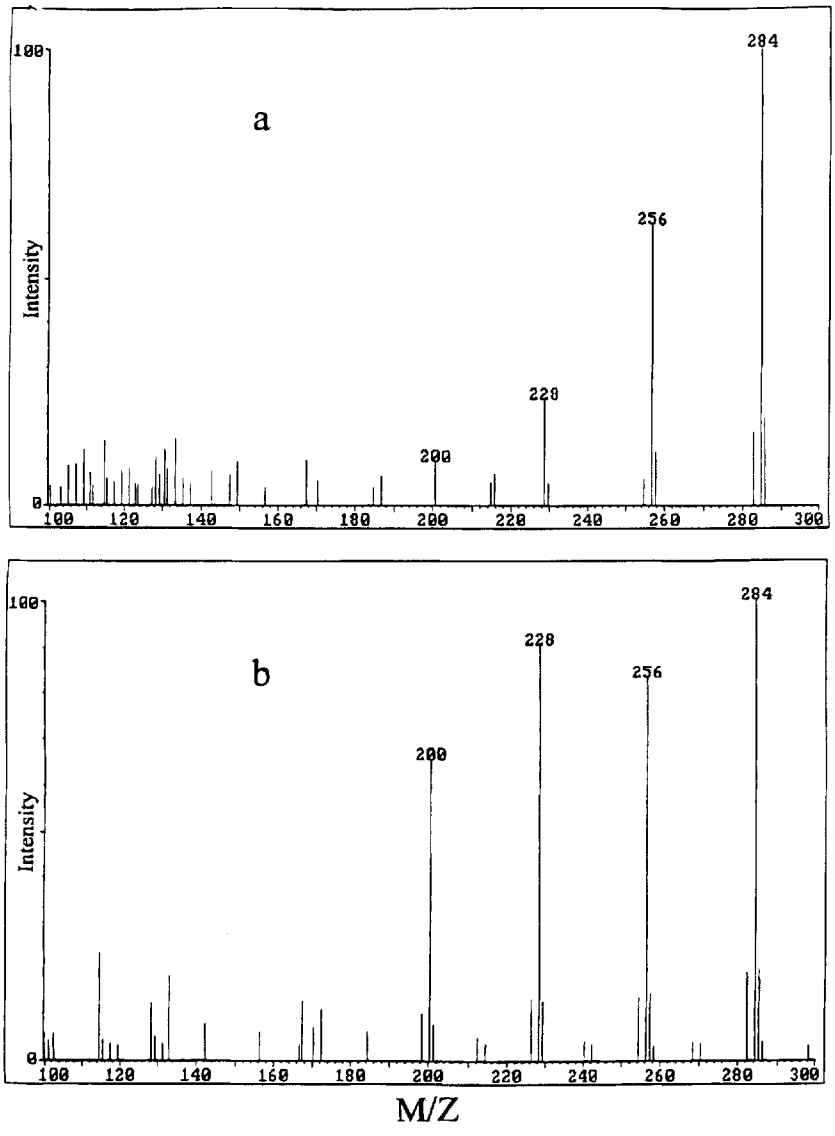

Figure 5. Positive LSI mass spectra of sample solutions containing 8×10^{-6} M each of decyltrimethylamine (*m/z* 200), dodecyltrimethylamine (*m/z* 228), tetradecyltrimethylamine (*m/z* 256) and hexadecyltrimethylamine (*m/z* 284) in methanol. The sample solution was applied directly on the surface of (a) a diglycerol matrix at room temperature and (b) a liquid nitrogen-frozen diglycerol matrix.

the spectral variations within a series were much smaller and the trends were always the same. It was found that the deviations of the signal intensity of each analyte from unity depend on the conditions of sample preparation and how well the matrix is cooled.

Solutions containing series of primary amines (octyl-, dodecyl-, tetradecyl-, hexadecyl- and octadecylamines) were also examined in the same way. Since the analyte molecules were not precharged, an ion–molecule reaction for proton transfer is required to form the pseudomolecular ion (MH^+; M refers to the analyte molecule) during LSIMS.[24] Nevertheless, owing to their structural similarity, it is expected that the efficiency of proton transfer (or gas-phase basicity) among the molecules will be similar. The LSI mass spectra obtained from the diglycerol matrix at room temperature and liquid nitrogen-frozen diglycerol are showing in Fig. 6(a) and (b), respectively. It can be seen when the frozen diglycerol matrix is used the signal intensity of the analytes is inversely proportional to their surface activity. The explanation for this unusual behaviour may lie in the difference in the solubilities of the primary amines on the matrix surface at low temperature. It is known that degree of solubility of a compound in liquid solution decreases with decrease in temperature. Since the temperature of the matrix is kept low, the analyte might precipitate rapidly from the solution. It is known that in a polar solvent, solubility decreases with increasing alkyl chain length of the analyte. Therefore, as the temperature decreases, the amine with the longest alkyl chain ($C_{18}H_{37}NH_2$) in the solution became least soluble. The decrease in solubility of the analytes at low temperature results in a decrease in the amount of the analyte in the solvated form and thus their signal intensity in the LSI mass spectra.[25].

Since the solubility of a precharged quaternary amine is much higher than that of a primary amine, solutions containing quaternary amines would be expected to behave totally differently. Although there was no direct evidence for this speculation, we observed rapid particle formation from the supersaturated solution containing hexadecylamine in water when the solution was dipped

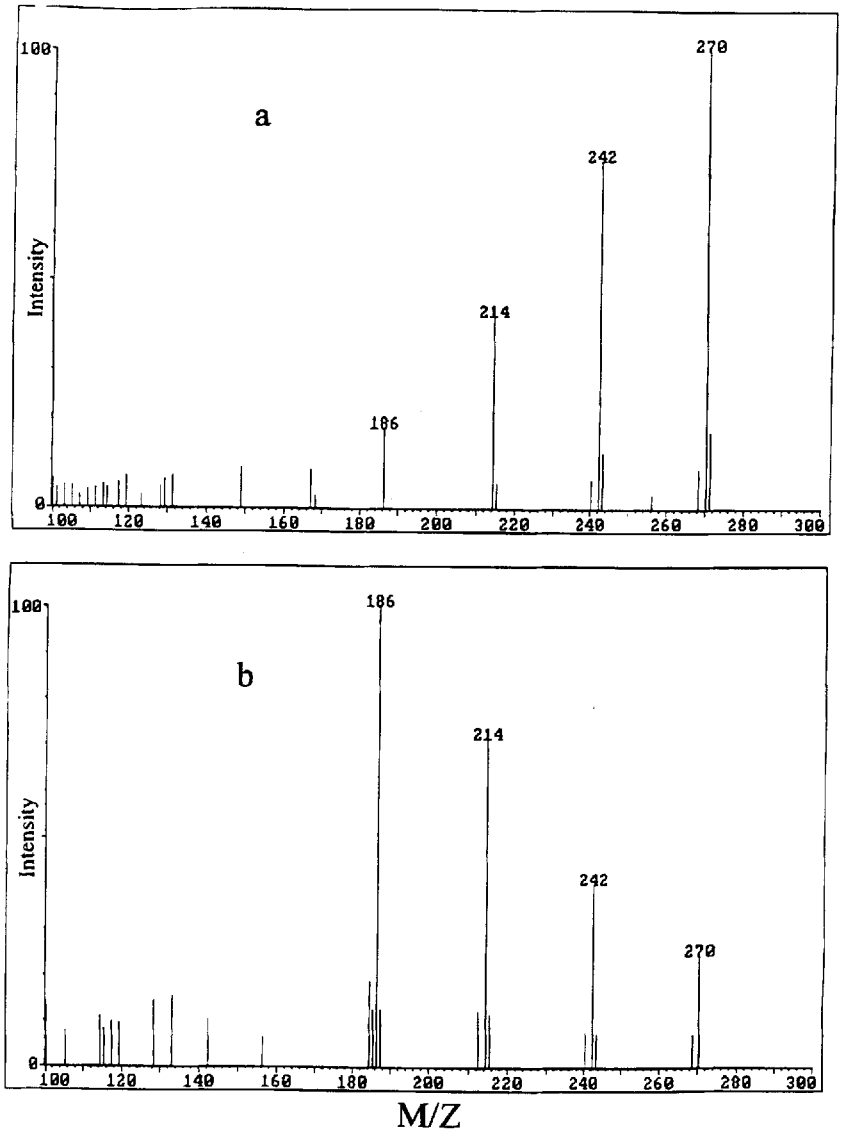

Figure 6. Positive LSI mass spectra of a sample solution containing 8×10^{-6} M each of decylamine (*m/z* 186), dodecylamine (*m/z* 214), tetradecylamine (*m/z* 242) and hexadecylamine (*m/z* 270) in the methanol. The sample solution was applied directly on the surface of (a) a diglycerol matrix at room temperature and (b) a liquid nitrogen-frozen diglycerol matrix.

into an ice-bath. The rate of particle formation for a supersaturated solution containing hexadecyltrimethylammonium bromide was much slower than that of the primary amine.

CONCLUSION

By absorbing gaseous ammonia molecules directly on the surface of a nitrogen frozen glycerol matrix, a good LSI mass spectrum showing strong NH_4^+ and (glycerol)NH_4^+ ion signals can be obtained. Good LSI mass spectra of volatile primary amines can also be obtained by directly applying the analyte solution (in methanol) on the surface of the nitrogen-frozen glycerol matrix. Since the frozen-glycerol matrix in the near-surface region is melted by the sample solution, the viscosity of the matrix in this region is suitable for LSIMS analysis. However, the temperature in the bottom part of the matrix is still low and the volatile analyte will then be retained on the surface. It was also found that, in much the same way, the LSIMS signals of a series of quaternary amines with different surface activities were nearly identical. The observation of elimination of the surface activity effect among the analytes on their LSI mass spectra is mainly due to the blockage of mass transport processes in the matrix under very low temperature and high viscosity conditions. The technique can potentially be used for rapidly detecting and identifying low-volatile organic components in commercial products such as cologne, perfume, cosmetics and food. The differences in the relative response of a series of the analyte ions in the LSI mass spectra are also expected to be small. The mass spectra obtained in this way can be used as the fingerprints to show differences in composition among different samples.

Acknowledgement

The authors express their appreciation for the financial support of this research by the National Science Council of the Republic of China.

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