Liquid Ionization Mass Spectrometry of Involatile Organic Compounds: Use of a Needle Electrode and Matrix

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Metastable argon atoms at atmospheric pressure were used to ionize organic compounds and an emitter for field desorption was used as a sample holder. The effect of electric field, temperature and additives were investigated for involatile compounds like nucleosides. High voltage applied to the emitter and a matrix increased the abundance of M+ ions significantly and long-lasting good mass spectra were obtained. A needle emitter was better than a silicon emitter and Nujol (liquid paraffin) as a matrix was better than glycerol for thermolabile compounds having small proton affinities such as guanosine and creatine.

1. Introduction

In recent years, involatile and thermolabile organic compounds have been investigated successfully by various types of mass spectrometry, such as field desorption (FD), plasma desorption, secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB), atmospheric pressure ionization (API) and several direct exposure techniques. There are, however, still many compounds whose mass spectra can not be obtained satisfactorily using any of these techniques.

We have developed a method which we call liquid ionization (LI), for ionizing trace amounts of organic compound present as a liquid or in solution at atmospheric pressure. The method was applied to an ion detector and a mass spectrometer. Results were good for low volatility compounds and some involatile ones like amino acids, but were not satisfactory for involatile and/or thermolabile compounds like poly-saccharides.

The method was investigated for the purpose of obtaining good mass spectra of involatile compounds and of understanding the mechanisms of ionization and desorption. In this paper, metastable argon pro-

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duced at atmospheric pressure was used as the ionizing species and a high voltage was applied to a probe containing the sample. A silicon emitter for FD, a filament and a needle for sewing were examined as the sample probe and the effect of additives (solvent and matrix) was also investigated.

2. Experimental

A modified quadrupole mass spectrometer (ANELVA TE 600 GC/MS) equipped with the ion source shown in Fig. 1 was used. Argon (carrier gas; 300 ml/min) at atmospheric pressure was ionized by a corona discharge between a needle electrode-1 and a counter electrode-2. Charged species were eliminated by connecting electrodes 2 and 3 to the earth, so that only metastable argon ($\text{Ar}^*$) produced in the carrier gas can flow into the ionization chamber and ionize a liquid sample deposited on the sample probe. When using a silicon emitter (JEOL made) as the sample probe, $1 - 2 \mu l$ of sample solution ($10^{-2} - 10^{-3} \text{M}$) is deposited on the emitter. On the other hand, when using a needle, $1 - 2 \mu g$ of solute is mixed with $1 \mu l$ of a matrix such as glycerol and less than one tenths of the mixture is deposited on the top of an ordinary sewing needle which is commercially available. The sample is heated by a DC current through the silicon emitter or by means of a tungsten wire surrounding the needle. Compounds whose ionization energies are below 11.72eV which is the internal energy of $\text{Ar}^* (3\text{P}_2)$, are ionized according to:

![Fig. 1. Schematic diagram of ion source of liquid ionization mass spectrometer.](image-url)
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\begin{align*}
    & \text{Ar} + e^- \xrightarrow{\text{Corona discharge}} \text{Ar}^+ + e^- \quad \quad (1) \\
    & \text{Ar}^+ + M \rightarrow M^+ + e^- + \text{Ar} \quad \quad (2) \\
    & \text{Ar}^+ + nM \rightarrow (kM + H)^+ + (nM - H)^- \\
    & \quad + (n-k-M) + \text{Ar} \quad \quad (3) \\
    & \text{S}_2\text{H}^+ + nM \rightarrow (kM + H)^+ \\
    & \quad + (n-k)M + xS \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (4)
\end{align*}
\]

The major processes in this method are thought to be reactions (3) and (4). Reaction (3) could be called slow atom bombardment. When using a solvent or matrix (S), reaction (4) must be the major process and \(\text{S}_2\text{H}^+\) is produced by reaction similar to (3) in which M is replaced by S. In the case of Nujol as the matrix, it has not yet understood that what the reactant ions are, \(\text{S}_2\text{H}^+, \text{S}^+\) or some other ions. The number k of observed ions is generally 1 and 2 for involatile compounds. Ions produced on the emitter are desorbed from the surface when heat and high voltage is applied to the emitter. These flow into the vacuum region (∼10⁻⁵ Torr) through a pinhole (30µm) and are analysed by the quadrupole mass spectrometer. Shimadzu's microcomputer data processing system (GCMSPAC 90) and a pen recorder were used to record mass spectra. Mass spectra between \(m/z\) 10 and 600 were scanned in 10 seconds with the former. The largest mass measurable was 1000 using an Extranuclear Laboratories’ quadrupole power supply (±011 – 15). Argon (99.99%) was purchased from the Takachiho Trading Co. and reagent chemicals were used as purchased from Tokyo Kasei Co.

3. Results and Discussion

Heating is required to observe ions from compounds normally considered to be

![Mass spectra of adenosine](image)

Fig. 2. Mass spectra of adenosine.

a) Mass spectrum in one scan using a silicon emitter (0.5 µg adenosine/1 µl methanol).
b) Summed mass spectrum of seven scans (others are the same as in a).
c) Using a needle with glycerol.
d) Using a needle with Nujol.
involatile. At optimum heating, a high voltage (V<sub>k</sub>: 1000 – 1200 V) applied to the silicon emitter increases the ion current more than 100 fold compared to that at emitter voltage of 200 V as reported previously. Rapid heating with an optimum emitter current at emitter voltage (V<sub>k</sub>) of 1100 V gave a moderately good mass spectrum as shown in Fig. 2a for adenosine. Such a spectrum, however, was observed only for a short period (10–60 s) and soon fragment ions increased to give the mass spectrum as shown in Fig. 2b which is the summed mass spectrum of seven scans.

It was found that the position of the emitter with respect to the pointhole had a significant effect on ion abundance and an ordinary sewing needle was better than the silicon emitter, especially when a matrix was used. Optimum position of the needle in the ion source can be fixed easily and maximum ion current of MH<sup>+</sup> is obtained at a needle voltage (V<sub>k</sub>) of around 1000 V. Use of a matrix increases the abundance of MH<sup>+</sup> ions remarkably, resulting in a long-lived mass spectrum as is observed using the FAB technique when glycerol is used as the matrix. In our method, glycerol produced a good mass spectrum for adenosine (Fig. 2c) which lasted for five minutes or so, but fragment ions of mass 136 (BH<sub>3</sub><sup>+</sup>) and ions from glycerol (G<sub>2</sub>H<sup>+</sup>, BHG<sup>+</sup>) were also observed and increased in later scans. Nujol was found to be a better matrix than glycerol. Nujol is a mixture of liquid paraffins (d=0.88–0.89) used commonly in infra-red spectroscopy. With Nujol, a stable MH<sup>+</sup> peak observed was for more than ten minutes without any other peaks except the M<sub>2</sub>H<sup>+</sup> ion peak (Fig. 2d).

In the case of cytidine, more fragment ions were produced than in the case of adenosine, although the base peak was due to MH<sup>+</sup> ions. As cytidine was not soluble in Nujol, a small amount of water added to the sample resulted in a better mass spectrum (Fig. 3b) when compared to that obtained with Nujol only. More fragment ions (BH<sub>3</sub><sup>+</sup> ......B<sub>3</sub>H<sup>+</sup>) were observed with glycerol (Fig. 3a). Dimeric ions, M<sub>2</sub>H<sup>+</sup>, and fragment ions of M<sub>3</sub>H<sup>+</sup>, (MHBH<sup>+</sup>) were also observed.

![Mass spectra of cytidine.](image)

**Fig. 3.** Mass spectra of cytidine.

a) Using a needle with glycerol.

b) Using a needle with Nujol.
It was difficult to observe the MH⁺ ion of creatine with glycerol as shown in Fig. 4b. The same applies to guanosine. Abundant (M–H₂O)⁺H⁺ ions (n = 1–3) were produced from creatine and abundant (BH)ₙ⁺H⁺ ions (B: base, n = 1–3) were produced from guanosine. In contrast, MH⁺ ions were observed as the base peak (Fig. 4a) by using Nujol. It is interesting to note that the ion at mass 150 corresponding to the protonated molecule of the compound used which includes one water molecule of crystalization, are observed as shown in Fig. 4a.

The role of the matrix is a proton donor, a solvent for solute molecules and/or ions, and a holder of sample in the right position. It is likely that these are just the same as those in the FAB technique. Ion current obtained from 10⁻⁷ g of solute is intense and long-lasting enough for recording mass spectra even by a pen recorder.

4. Conclusion

A needle emitter and a matrix of Nujol is very useful as a sample holder in this method. Concentrated electric field at the top the needle assists desorption of ions and focusing ions on the pinhole, resulting in stable mass spectra with abundant MH⁺ ions at some optimum temperature. Long-lasting, good mass spectra can be obtained with Nujol (liquid paraffins) which is better than glycerol, probably because the proton affinities of alkanes are low when compared with all other types of compounds and the interaction between alkane and other compounds is generally weak.

Advantages of this (LI) method are: soft ionization producing abundant MH⁺ ions, ease of sample handling, free use of additives (matrix, solvent and so on), very low back ground, and high sensitivity.

References

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Keywords
- Liquid ionization mass spectrometry
- Atmospheric pressure ionization
- Nucleosides
- Slow atom bombardment
- Field desorption
- Matrix