Infrared Laser Desorption Ionization Mass Spectrometry

Introduction

UV-MALDI MS requires the addition of a light-absorbing matrix to facilitate intact ionization of sample material. Matrix addition not only complicates sample preparation, which sometimes requires a skilled technician, but also interferes with low mass analysis due to ionization of the matrix. However, certain classes of compounds can be directly desorbed and ionized without matrix addition through IR vibrational absorption of functional groups in the compound. These ionized compounds can then be detected with no fragmentation using time-of-flight mass spectrometry. In this application note, matrix-free IR LDI MS of small molecules and peptides using a tunable mid-IR OPO laser system will be shown.

Experimental conditions

A mixture of 16 peptides (Table I) was prepared in 1:1 acetonitrile/1% TFA. A 5 µL aliquot (6.75 pmol/peptide) of the solution was deposited on a Si target and dried to a thin film using a heat gun. Likewise, 5 µL of a Kirkland Signature acetaminophen pill (5 mg) in 1 mL of 3:1:1 1% TFA/methanol/acetone was deposited on a Si target and dried to a thick film using a heat gun. Each Si target was inserted into a custom-built time-of-flight mass spectrometer and desorbed and ionized with 0.24 J/cm^2 of mid-IR pulsed laser light using an IR Opolette running at 2 Hz.

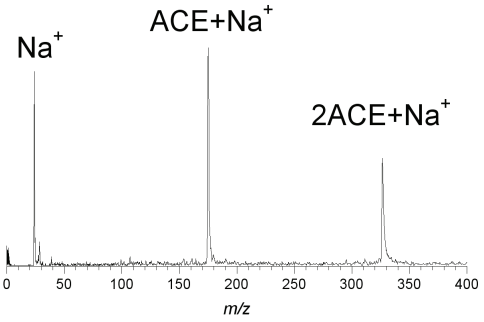

Figure 1. IR LDI MS of acetaminophen (ACE) tablet (λ = 3.0 µm, 5 shot average)

Results

Figure 1 shows the results from the direct mid-IR ionization of an acetaminophen tablet. Without the addition of matrix, only the sodium, sodiated analyte and sodiated analyte dimer ions are detected in the low mass region.

Table 1

Peptide Name	MW
Angiotensinogen Frag 11-14	481.6
Bradykinin Frag 1-5	572.7
Bradykinin Frag 1-7	756.9
[des-Arg^1]Angiotensin III	774.9
[Sar^1,Ile^7]Angiotensin	812
[Ile^7]Angiotensin III	897.1
Bradykinin Frag 1-8	904
Angiotensin III	934
[Sar^1,Thr^8]Angiotensin II	956.1
[Val^5]Angiotensin II	1032
Angiotensin II	1046.2
Bradykinin	1060.2
[Val^5]Angiotensin I	1282.5
Angiotensin I	1296
Substance P	1347
Renin Substrate Tetrapeptide	1759

An example of direct mid-IR ionization of a peptide mixture is show in figure 2. Protonated as well as sodiated and potassiated adducts were detected for each peptide.

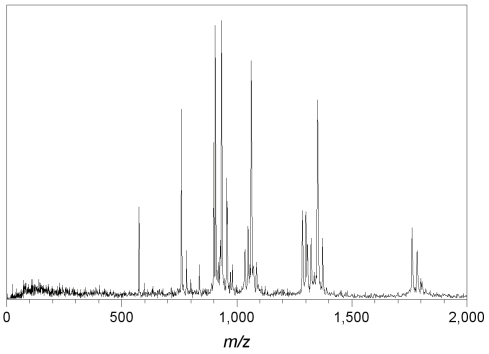

Figure 2. IR LDI MS of 16 peptide mixture (λ = 2.94 mm, 5 shot average)

Conclusions

Samples of peptides and small molecules were successfully ionized without fragmentation using mid-IR laser light and no added matrix.

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