Desorption ionization methods essay

Pharmaceutical science

Desorption ionization methods owning a powerful capability in pharmaceutical field in which the ionization sources provided by the respective mass spectrometers was able to minimize the damage causing any variations in molecular structures of the samples (Monagas, Quintanilla-López, Gómez-Cordovés, Bartolomé, & Lebrón-Aguilar, 2010). The prevention can be done by using ideal matrix mixed with the analytes, owning properties of strong absorption, good mixing and having low vapor pressure. With these properties the mass spectrometer are able more accurate in determine the intact molecular m/z value of the analytes.

MALDI-TOF MS

Huge numbers of researchers was reported a species that associate with various benefits in health known as proanthocyanidins , a polyphenols compounds which having properties of cardiovascular and neurodegenerative diseases prevention (Aron & Kennedy, 2008). Several authors were characterized proanthocynidins in both plants and non-plants foods by the application of MALDI-TOF MS in term different mode of detection and mass species. Two different mode of detection, reflectron mode and linear mode, have been well applied in proanthocynidins analysis. By using MALDI-TOF MS applying on proanthocynidins analysis owning a great advantages in minimize the difficulty in interpret the spectra in which it used single-charged molecular ions for detection that can eliminate those impurities peak that generate by other sources (Monagas, Quintanilla-López, Gómez-Cordovés, Bartolomé, & Lebrón-Aguilar, 2010).

The proanthocynidins are essential in food plants and non-food plants sample. This review was provides three example for both plants that are available in journal article. For the food plants, apple juice procyanidins was detected by MALDI-TOF MS in linear mode by both $[M+Na]^+$ and $[M+K]^+$ had been well studies by Shoji, et al. (2006). The authors were concluded that the apple juice procyanidins was exit as B-type procyanidins and the observed mass of the species reported as $[M+K]^+$ are higher than $[M+Na]^+$. Other foods plant, Grape seeds, was reported by Krueger, et al. (2000) as $[M+Na]^+$ in both reflectron and linear mode. The type of proanthocyanidin was being detected are B-type procyanidins and galloylated (esterified form) in various range of degree of polymerization (DP). It was found that the linear mode can be detected up to DP 11 while reflectron mode only can detect up to DP 9. Besides, Krueger, et al. in 2003 was reported another foods plant, Sorghum (*Sorghum bicolor (L.) Moench),* as $[M+Cs]^+$ in the reflectron mode was able to detect A- and B-type procyanidins and prodelphinidins. Due to the complexity of this food plant, the authors enable the detection up to DP9 containing up to 5 A-type linkages and confirming the abundance of the linkages in Sorghum (Krueger, Vestling, & Reed, 2003).

On the other hand, non-food plants proanthocynidins can also applied by MALDI-TOF MS. However, in the application of non-food plants, unlike application in food plants, Hedqvist, et al. (2000) was reported the *Lotus corniculatus* (var. Fargus) have presented B-type procyanidins and prodelphinidins by the application in both reflectron and linear mode were detected as $[M+Na]^+$. By establishing reflectron mode, B-type procynanidins and prodelphinidins in acetylated form in bark of *Pinus radiata*

were reported by Ku and Mun (2007). Besides, profisetinidins and prorobinetinidins in heartwood of Quebracho (*Schinopsis balansae*) were reported by Vivas, et al. (2004).

Table 1: Characterization of proanthocyanidins from both food plants and non-food plants by MALDI-TOF MS analysis

Materials	Substrate	Mode	Mass specie	Observed mass	Proanthocyni din type	Referen ce
Food plants	Apple juice	Liner	[M+ Na] + [M+ K] +	1754-2907 1770-2923	B-type procynanidin s	Shoji et al. (2006)
Grape seeds	Reflectro n Liner	[M+Na] + [M+Na] +	601- 2618 600- 3349	B-type procynanidin s, galloylated	Krueger et al. (2000)	
Sorghum (*Sorghu m bicolor (L.)*	Reflectro n	[M+Cs] +	1285 - 2759	A- and B-type procynanidin s and prodelphinidi	Krueger et al. (2003)	

Moench)				ns		
Non-food plants	*Lotus corniculatus (* var. Fargus)	Linear and reflectron	[M+Na]+	1177-1817	B-type procynanidins and prodelphinidins	Hedqvist et al. (2000)
Bark of *Pinus radiata*	Reflectron	[M+Na]+	1020-4067	B-type procynanidins and prodelphinidins (acetylated form)		Ku and Mun (2007)
Heartwood of Quebracho (*Schinopsis balansae)*	Reflectron	[M+Na]+	841-2237	Profisetinidins and prorobinetinidins		Vivas et al. (2004)

FAB-MS

The application of FAB-MS in pharmaceuticals sector was baring an importance role in analyzing those nonvolatile compounds in yields abundant ions and detailed fragmentation data (Bartner, et al., 1997). Everninomicin-6 (EV-6) was reported as an oligosaccharide antibiotic by Bartner, et al. (1997). The authors were using previous studies, Everninomicin-D (EV-D), by comparing their fragmentation m/z value in order to well analyze the fragmentation. Besides, the paper also operated by using various types of matrices in order to illustrated more structurally informative fragment ions such as glycerol, thioglycerol, glycerol/thioglycerol, 3-nitro-benzyl alcohol (3NBA), and 3NBA+NaCl.

In the studies, the FAB spectra were yields a very weak protonated and a relatively low-abundance sodiated molecular ions at m/z 1335 and 1357 respectively. The authors were emphasize that the matrix, NaCl doped 3NBA was producing the best result among the matrices that they were used. The spectra were able to shown a clearer enhancement of the sodiated molecular ion at m/z 1357 and the authors also able to determine several series of the molecular fragmentation. This make the spectra more essential in define the structurally informative ion constituent. However, negative-ion FAB-MS had been investigated by the authors for the structural analysis perform by using DMSO-3NBA matrix and produced abundant molecular ion at m/z 1333 and a series of cleavage of ions peak.

Table 2: The relatively abundance molecular ions peak of the Everninomicin-6 (EV-6) in DMSO solvent

Matrices	Mass	Observed	Assignation

	specie	mass	
50: 50 glycerol/thioglycerol (gly/thio)	$[M+H]^+$	1335 1357	-very weak protonated molecules ion -low-abundance sodiated molecular ion
3NBA + NaCl	$[M+Na]^+$	1357	-abundant sodiated molecular ion
3NBA	$[M-H]^-$	1333	-abundant molecular fragment ion

SIMS

Applications of SIMS in pharmaceutical sector are used to detect the surface morphologies of the analyte. In order further improve the detection limit, Chen, et al. (2011) research was using C_{60} cluster ion sources. The studies were done by the event-by-event bombardment/detection mode and providing benefits which allowed the detector very narrow length (~10nm) molecules. Chen, et al. (2011) were reported that this mode was increased the sensitivity of the detection toward the closer distances between nanoparticle probe and amino acid sites of an antibody.

It was reported that the gold nanoparticles (AuNPs) was modified in which the antiCD4 cooperate to the AuNPs and immobilized on the cell for analyze. It was reported that the negative ions that cleavage by the molecules in the range of m/z 30 to 120 were indicating the present of the antibodies on the

cell. Besides, m/z 197 and m/z 223 corresponding to Au^- and $AuCN^-$ respectively, were shown the importance of the peak which indicating the immobilization was successful. On the other hand, the ions source of C_{60} caused the impact on the lipid membrane region where the fragmentation palmitate ($C_{16}H_{31}O_2^-$) and oletate ($C_{18}H_{33}O_2^-$) at m/z 255 and 283 respectively had occurred.

Table 3: The co-emitted secondary ions and observed mass of AuNPs-antiCD4 labeled cell surface analyzed with C_{60} ToF-SIMS

Detected species	Co-emitted secondary ions	Observed mass
AuNPs-antiCD4 conjugates	Au^-	197
	$AuCN^-$	223
Cell lipid membrane	$C_{16}H_{31}O_2^-$	255
	$C_{18}H_{33}O_2^-$	283