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A Novel Wire Desorption ElectroSpray/Glow Discharge Ionization Source for Fast Identification of a Broad Range of Compounds

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Overview

A novel ambient ionization mass spectrometry based on heating wire desorption and electrospray ionization & glow discharge ionization (WD-ESI/GDI) was developed to characterize chemical compounds with different polarities and thermal stabilities at atmospheric pressure.

Introduction

A novel ambient ionization source, WD-ESI/GDI source, was developed to analyze mixtures containing analytes with different polarities and thermal stabilities in different phases at atmospheric pressure. WD-ESI/GDI had four significant advantages: 1) low thermal capacity - fast heating & cooling; 2) self-cleaning; 3） simple operation for thermal desorption without carrier gas; 4) a universal ion source for analytes with different polarities, state and thermal stability. Figure 1 displays the desorption and ionization processes occurred in WD-ESI/GDI.

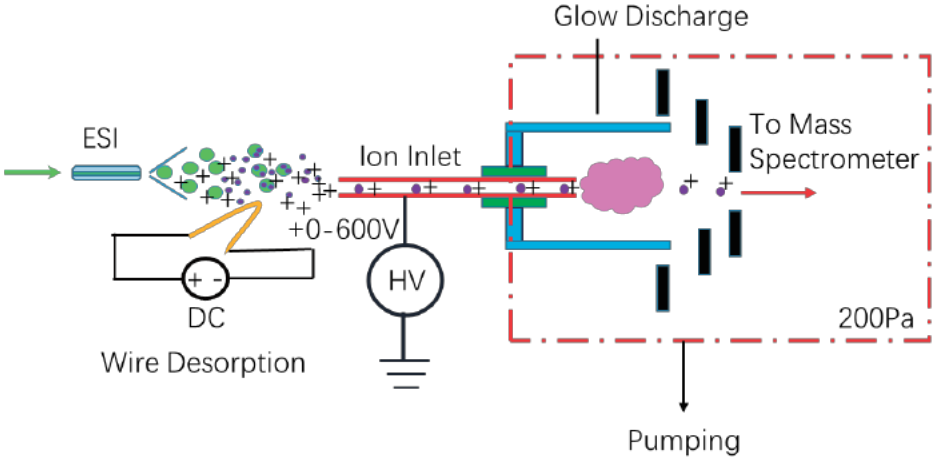

Figure 1　Schematic of WD-ESI/GDI desorption and ionization processes on LCMS8040

Instrument & Methods

The WD-ESI source was attached to a triple quadruple mass spectrometer (Shimadzu 8040, Japan) to detect the analyte. The WD-ESI source was composed of two parts: a heating wire desorption pen (i.e. thermal desorption unit) and ESI/GD ionization device. The temperature of the wire can be increased very rapidly to over 1000oC within seconds, and analytes can be desorbed from the sample solution or powder. Figure 2 shows the photographs of WD pen

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Figure 2 Photographs of WD pen

Table 1 Summary of Optimal Parameters in WD-ESI/GDI

	Parameter	Parameter optimal setting
WD-ESI	the electric current in wire	2.5A
	Electrospray high voltage	5 kV
	electrospray solvent flow rate	2μL/min
GDI	GDI current	0.6mA
	GDI voltage	600V

In WD-ESI, desorbed analytes are introduced into the micro-ESI plume and can interact with charged droplets to form analyte ions during the process of desolvation as shown in Figure 3. Alternatively, when non-polar species were analyzed, desorbed analytes can also interact with the plasma formed in a glow discharge located in an intermediate pressure region (200 Pa) downstream of the MS inlet. Figure 4 shows thermal image of WD pen while heating.

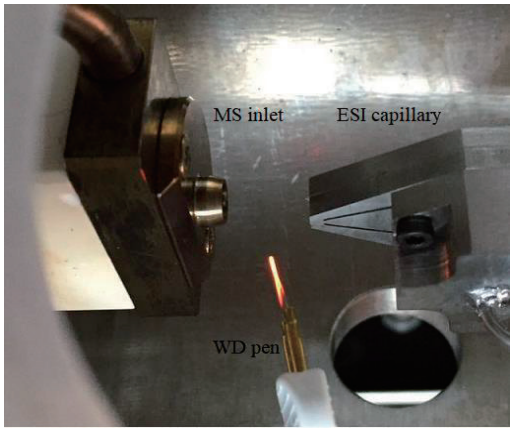

Figure 3 Photographs of inside of the WD-ESI source on LCMS8040

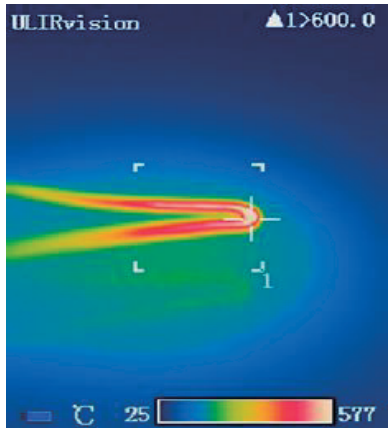

Figure 4 Thermo image of WD pen

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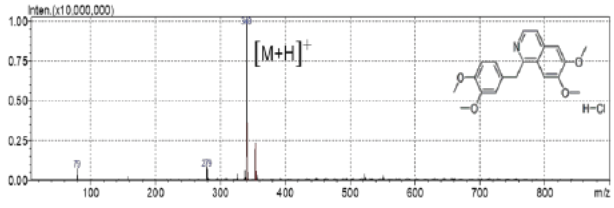
WD can thermally desorb not only substance with low polarity & high volatility but also some species with very high polarity & low volatility without decomposition during vaporization. To sample liquid sample, 2-5 μL of sample solution is deposited onto the bent tip of wire on the WD pen with micropipette. To sample solid sample, the wire is swept across the sample's surface for a short distance. For powder sample, the wire is quickly dipped and removed from the sample to collect the powders adhered on the wire.

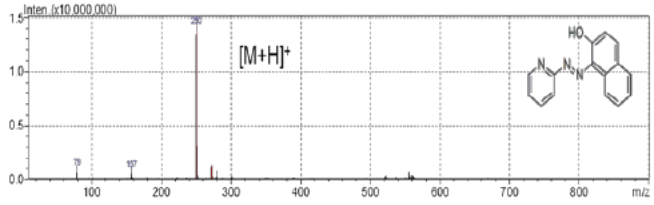
Experimental results

Analysis of the samples with different polarities, state and thermal stability

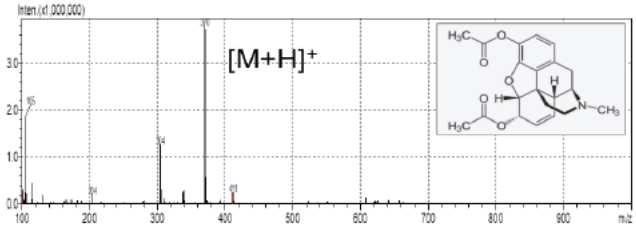
The application of WD-ESI/MS was demonstrated with the analysis of less polar compound and polar compounds in methanol aqueous solution (50:50, v:v). Figure 5 shows the spectra in different operating modes.



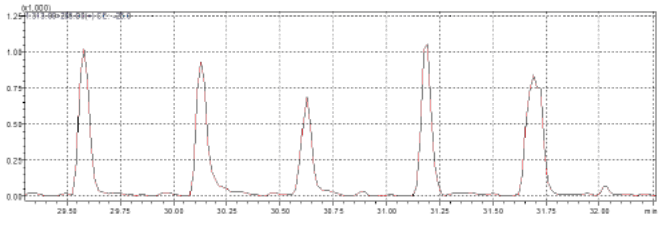
Papaverine hydrochloride in Q1 scan mode
(m/z: 340, $[M+H]^+$) (10 mg/kg)



1-(2-pyridinylazo)-2-naohthalenol in Q1 scan mode
(m/z: 250, $[M+H]^+$) (10 mg/kg)



Heroin in Q1 scan mode
(m/z: 370, $[M+H]^+$) (10 mg/kg)



10 pg Aflatoxin B1 in MRM mode
(m/z: 313>285)

Figure 5 Mass spectra with WD-ESI on LCMS8040

Rapidly identify different analytes in solid are the requirements for some application. WD-ESI/MS was also used to characterize powder compounds ion signal intensity as shown in Figure 6. The results reveal that WD-ESI/MS can be used to analyze chemical compounds in solid and liquid states and in different polarities.

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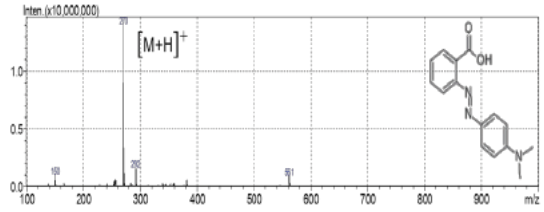
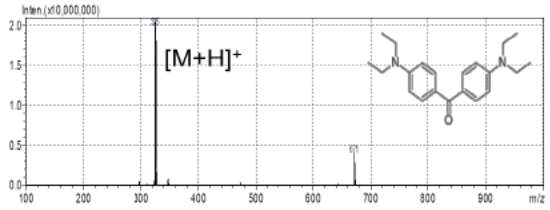


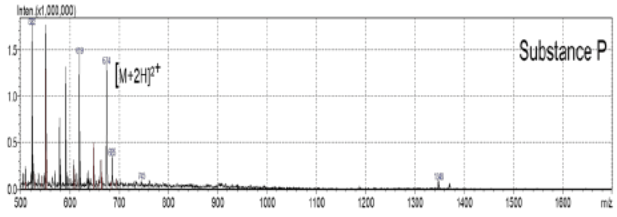
Methyl red in Q1 scan mode
(m/z: 270, $[M+H]^+$)



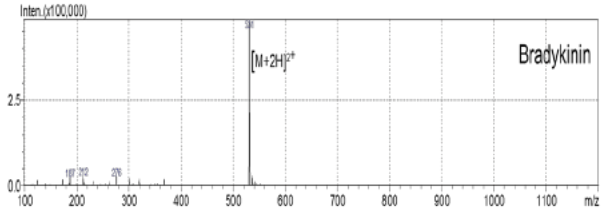
Bis(diethylamino)benzophenone in Q1 scan mode
(m/z: 325, $[M+H]^+$)

Figure 6 Mass spectra with WD-ESI/MS

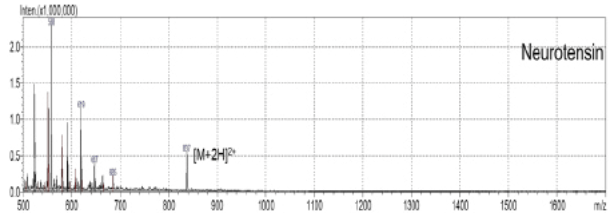
Figure 7 shows peptide spectra with WD-ESI. Small peptides solution can be applied on the wire before heating. When the wire was rapidly heated, the peptide solution will quickly splash and form tiny droplets. These droplets will then interact with those droplets from micro-ESI and form peptide ions after sufficient desovlation. Doubly charged analyte ions were detected as the predominant ion signal on the mass spectra including substance P (m/z 674, $[M+2H]^{2+}$), bradykinin (m/z 531, $[M+2H]^{2+}$) neurotensin (m/z 837, [M+2H]2+) and bivalirudin (m/z 1091, $[M+2H]^{2+}$).The singly charged substance P ion (m/z 1348, [M]+) was also detected. The results indicate that even the compounds with large molecular weight and poor thermally stable like peptides did not decompose in the WD-ESI source.



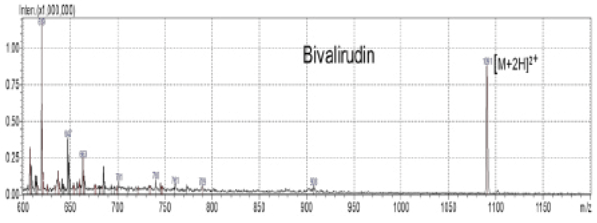
Substance P in Q1 scan mode
(m/z: 674, $[M+2H]^{2+}$) (100 mg/kg)



Bradykinin in Q1 scan mode
(m/z: 531, $[M+2H]^{2+}$) (100 mg/kg)



Neurotensin in Q1 scan mode
(m/z: 837, $[M+2H]^{2+}$) (100 mg/kg)



Bivalirudin in Q1 scan mode
(m/z: 1091, $[M+2H]^{2+}$) (100 mg/kg)

Figure 7 Analysis of polypeptides with WD-ESI/MS

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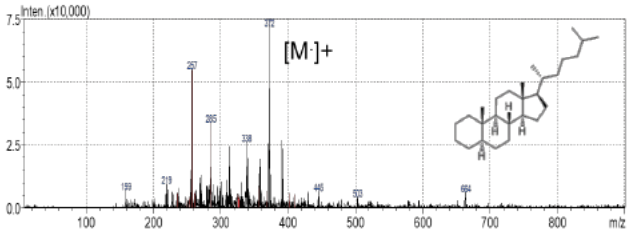
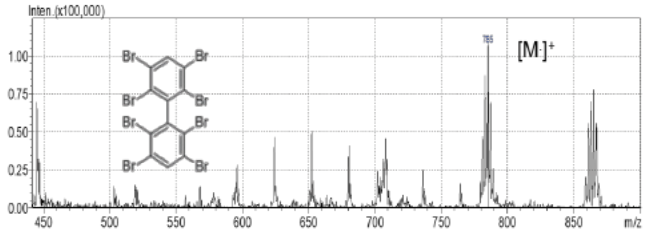
Analysis of the samples with non-polarity

GDI can extend the application of WD-ESI on rapid profiling of non-polar molecules. The performance of WD-GDI/MS in detection of 5α-cholestane (20 mg/L) in dichloromethane and octabromobiphenyl (20 mg/kg) in acetone was evaluated. But the same compounds cannot get the signals with WD-ESI.



5α-cholestane in Q1 scan mode
(m/z: 372, $[M.]^+$) (20 mg/kg)



Octabromobiphenyl in Q1 scan mode
(m/z: 785, $[M.]^+$) (20 mg/kg)

Figure 8 Analysis of non-polarities with WD-GDI on/MS

Analysis of small compound from peanut oil and polypeptide from polypeptide drug samples

To further demonstrate that WD-ESI/MS/MS can be used to detect trace analyte in the sample containing mixture compounds that quantitative analysis of AFB1 in peanut oil and bivalirudin in the polypeptide drug by WD-ESI/MS/MS was conducted, respectively. The WD-ESI requires little to no sample pretreatment during sample analysis. This makes the entire analytical processes extremely fast (less than 10 s) including sampling, desorption, ionization, and detection. The results are summarized in Table 2. The limit of detection (LOD) and quantification (LOQ) of AFB1 and bivalirudin can meet the requirements of food and drug safety.

Table 2 Summary of analysis of AFB1 in peanut oil and bivalirudin in drug with WD-ES/MS

	Analyte assigned value	Recovery/%	RSD/%	LOD	LOQ
AFB1	5 μg/kg	110	17.6	0.28μg/kg	0.28μg/kg
	10μg/kg	101	19.5		
	60μg/kg	104	18.9		
Bivalirudin	7 mg/kg	107	12.3	0.08 mg/kg	0.13 mg/kg
	14 mg/kg	112	9.7		

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Conclusions

A novel ambient ionization technique – WD-ESI/GDI was developed for detecting small organic compound and large biological compounds – polypeptide. WD-ESI/GDI owns four significant advantages: 1) low thermal capacity – fast heating & cooling; 2) self-cleaning; 3） simple construction of thermal desorption unit without carrier gas; and 4) universal for analytes with different polarities, state and thermal stability. The use of a direct sampling probe in WD-ESI/GDI makes the analysis of trace chemical compounds in solid powder and liquid possible. Trace AFB1 (ppb level) in peanut oil can be rapid determined by the WD-ESI/MS/MS. Furthermore, bivalirudin in ppb level in polypeptide drug can also be determined.

Acknowledgement

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Disclaimer: WD-ESI/GDI is intended for Research Use Only (RUO). Not for use in diagnostic procedures. Not available in the U.S.

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