

# Electrospray Ionization Using Wooden Tips

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# INTRODUCTION

Since the introduction of ESI in 1980s considerable efforts have been made to further improve the sampling and ionization of this technique.

Nanoelectrospray ionization (nano-ESI) allows softer ionization and requires smaller volume of samples.

Desorption electrospray ionization (DESI) and extractive electrospray ionization (EESI) have enabled direct analysis of complex samples with no or little sample preparation.

In the past 2 decades, noncapillary emitters have also been developed to avoid the clogging problem in conventional capillary based ESI.

Fenn attempted to generate ESI from a wicking element, e.g., cotton wire, and found the possibility of ionization from paper or a thin layer chromatography (TLC) plate.

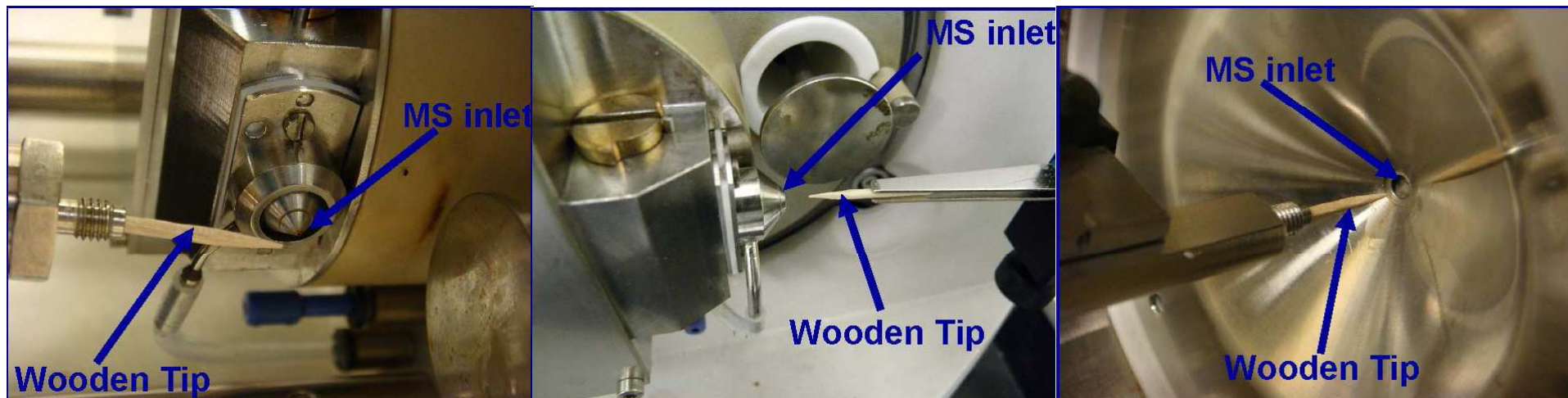
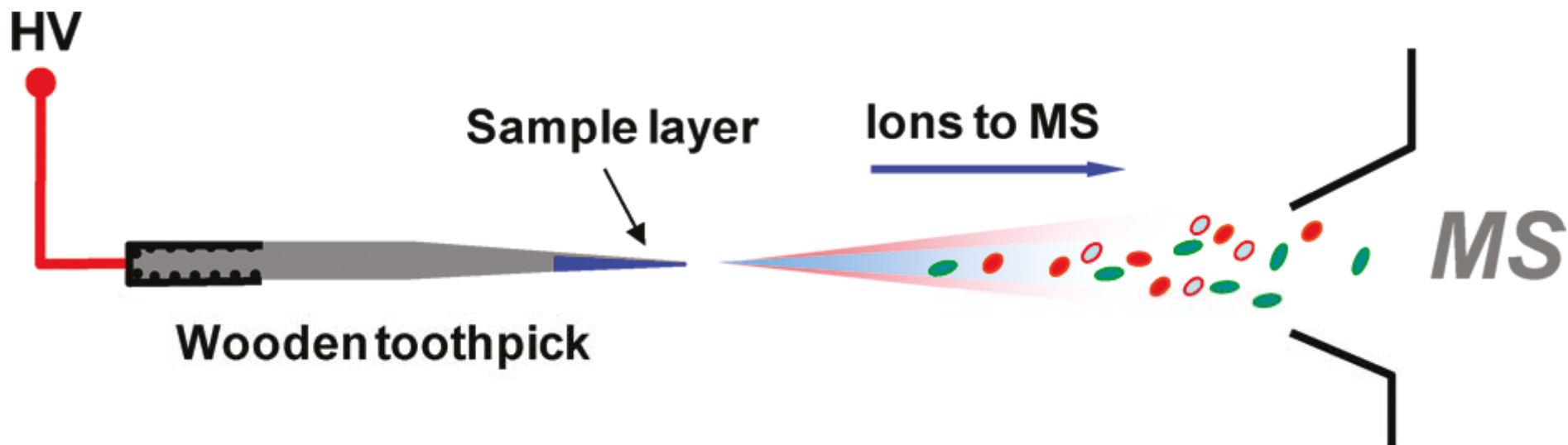
Copper wire, stainless steel needle, optical fibers wired with a copper or platinum coil, surface-modified glass rod and nanostructured tungsten oxide have been successfully developed as emitters for ESI.

Recently paper spray, which used paper as a medium for sample loading and ionization, was also introduced.

# EXPERIMENTAL SET-UP

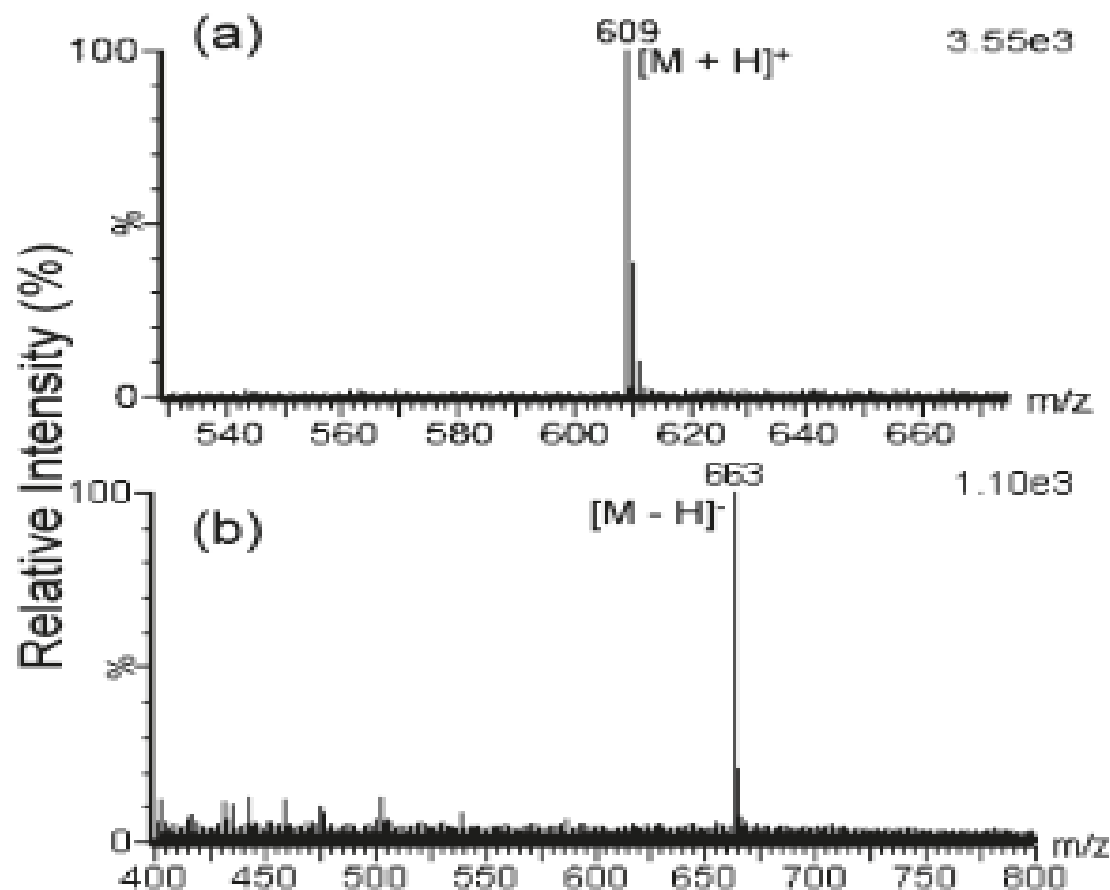
In this paper a new ionization method have been described using disposable wooden tips for loading and ionization of samples.

Wooden toothpicks with sharp end have been used for this purpose.



# RESULTS AND DISCUSSIONS

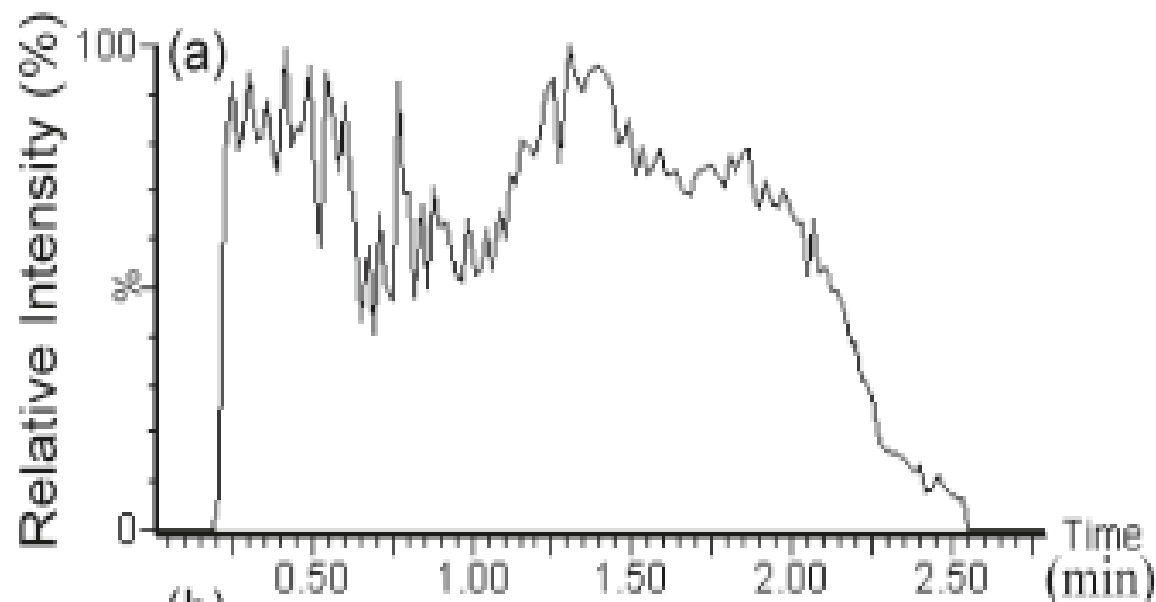
## Analysis of small molecules:



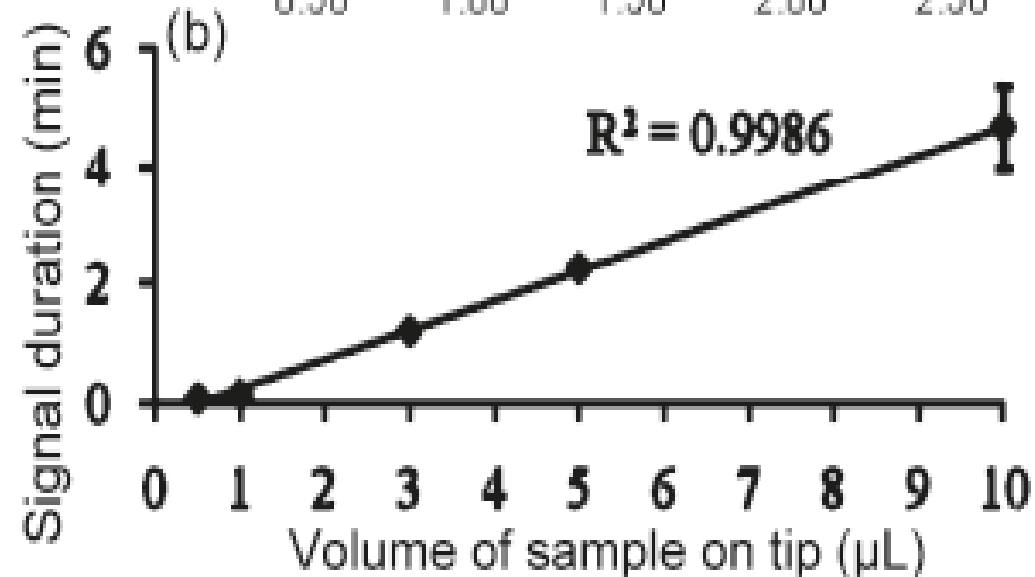
Positive mode spectrum of reserpine, 1 $\mu$ M solution

Negative mode spectrum of angiotensin I/II, 10 $\mu$ M

## Performance of the technique:

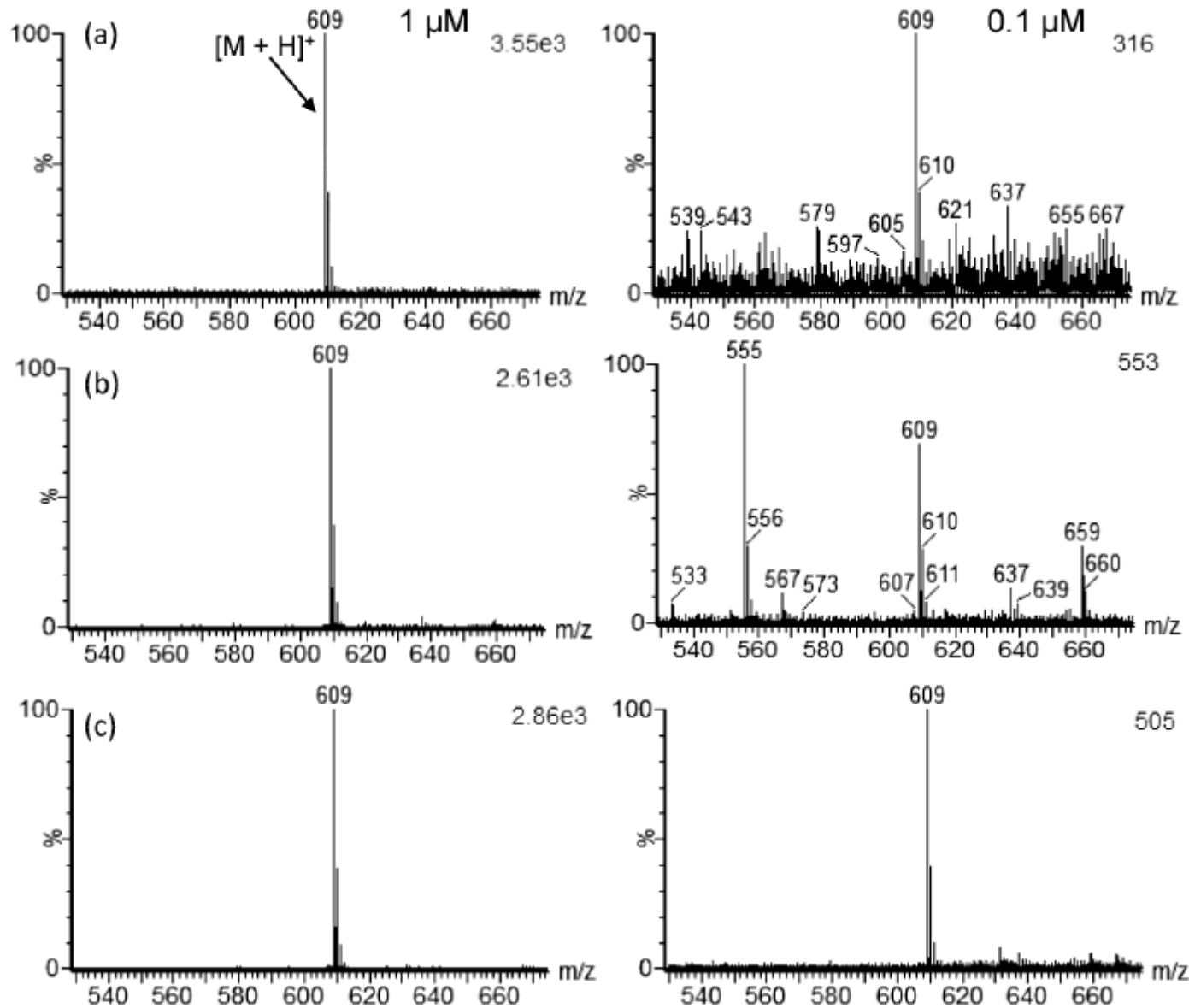


Total ion chromatogram for 5 $\mu$ L reserpine solution



Duration of signals of the reserpine solution with the volume of solution applied on the tip

# Comparison with paper spray and nano-ESI:



Wooden tip

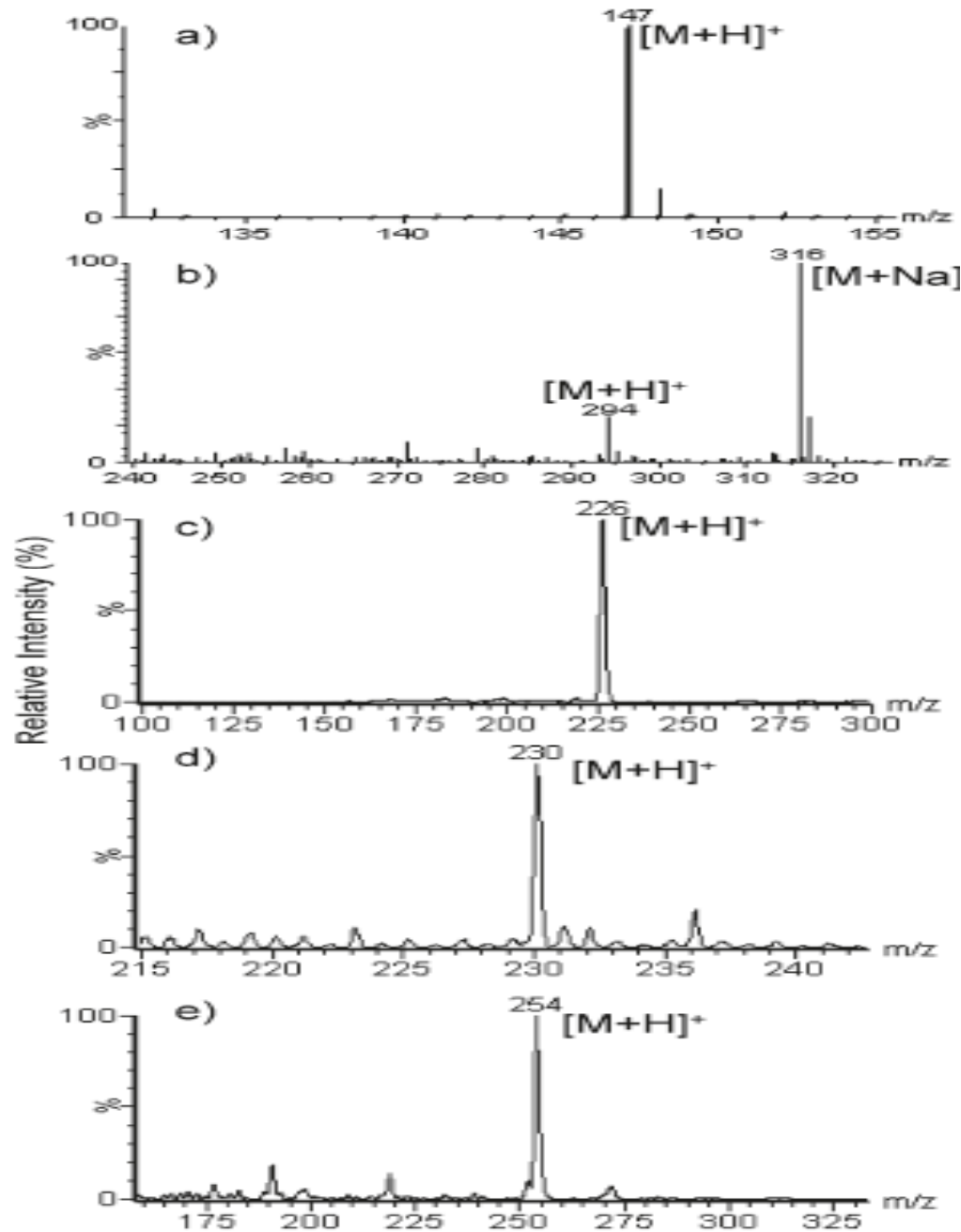
Paper spray

Nano-ESI

1 μM reserpine

0.1 μM reserpine

## Applicability to different compounds:



Lysine

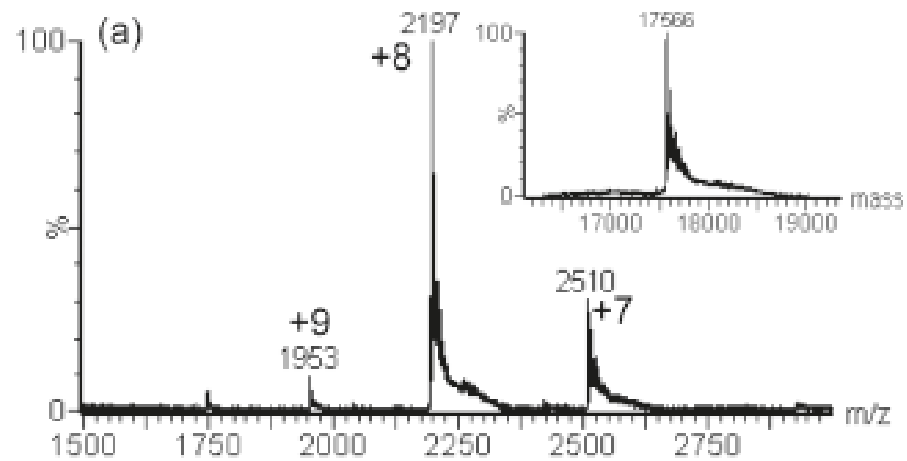
Gly-Ala-Phe

Methyl yellow

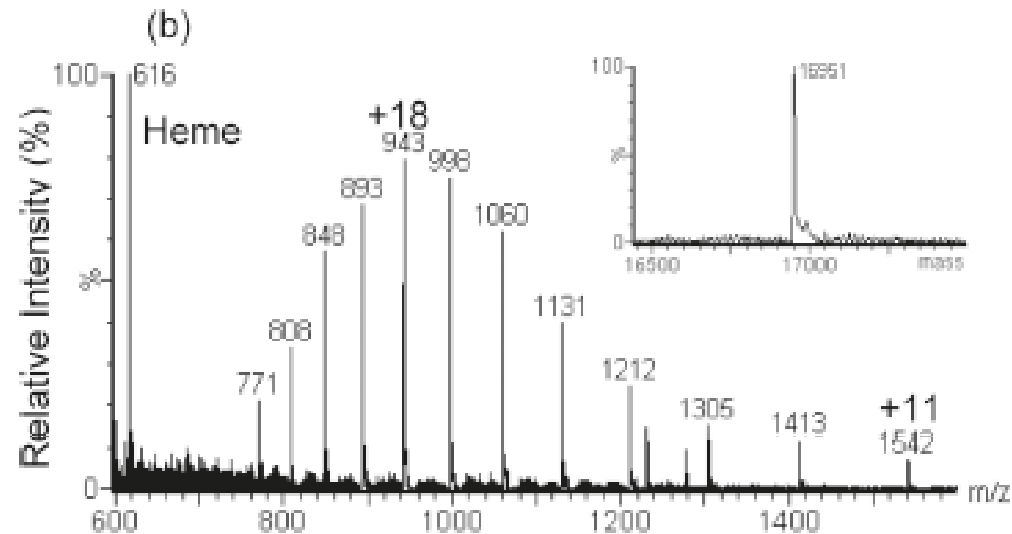
Dimethoate

Iron(II) acetylacetonate

## Analysis of proteins:



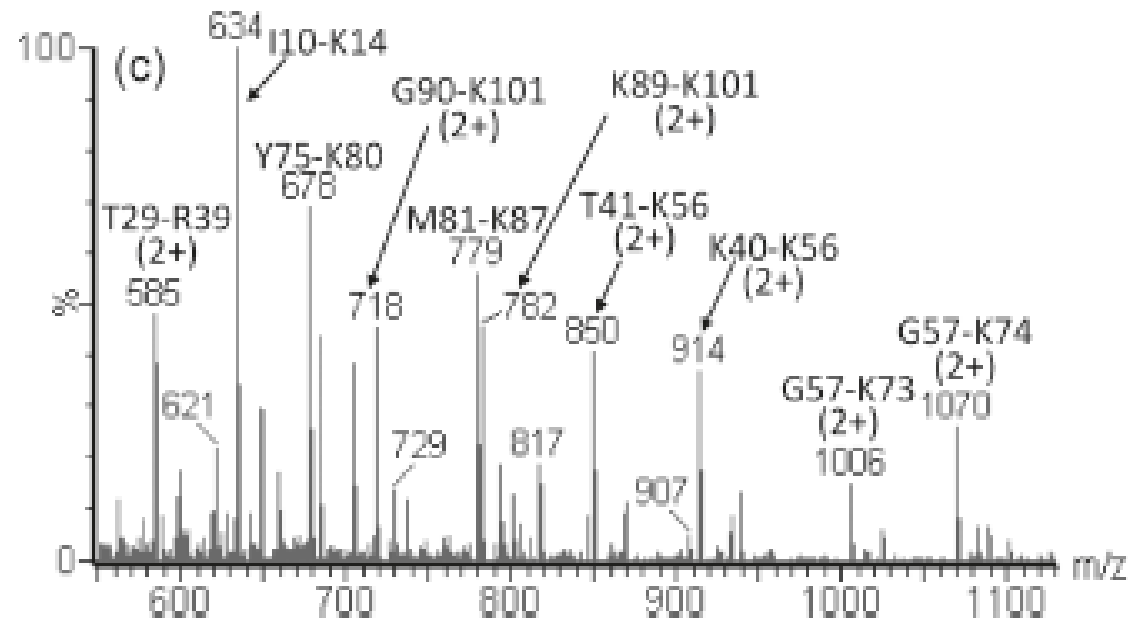
20  $\mu$ M myoglobin in  
20mM ammonium acetate



20  $\mu$ M myoglobin in ACN/20mM  
 $\text{CH}_3\text{COONH}_4$  (1/1) containing  
0.1% formic acid

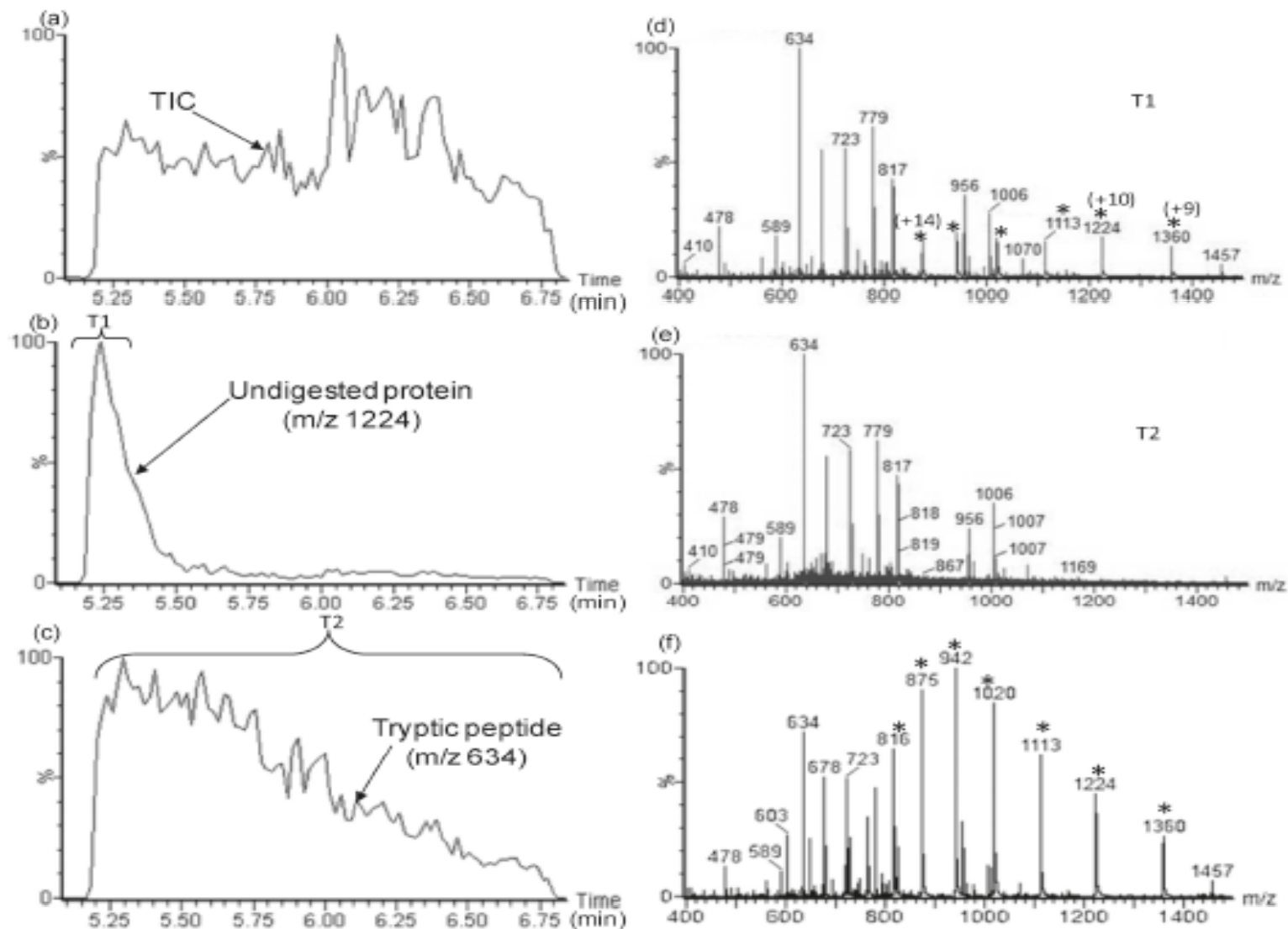


## Analysis of tryptic digests:



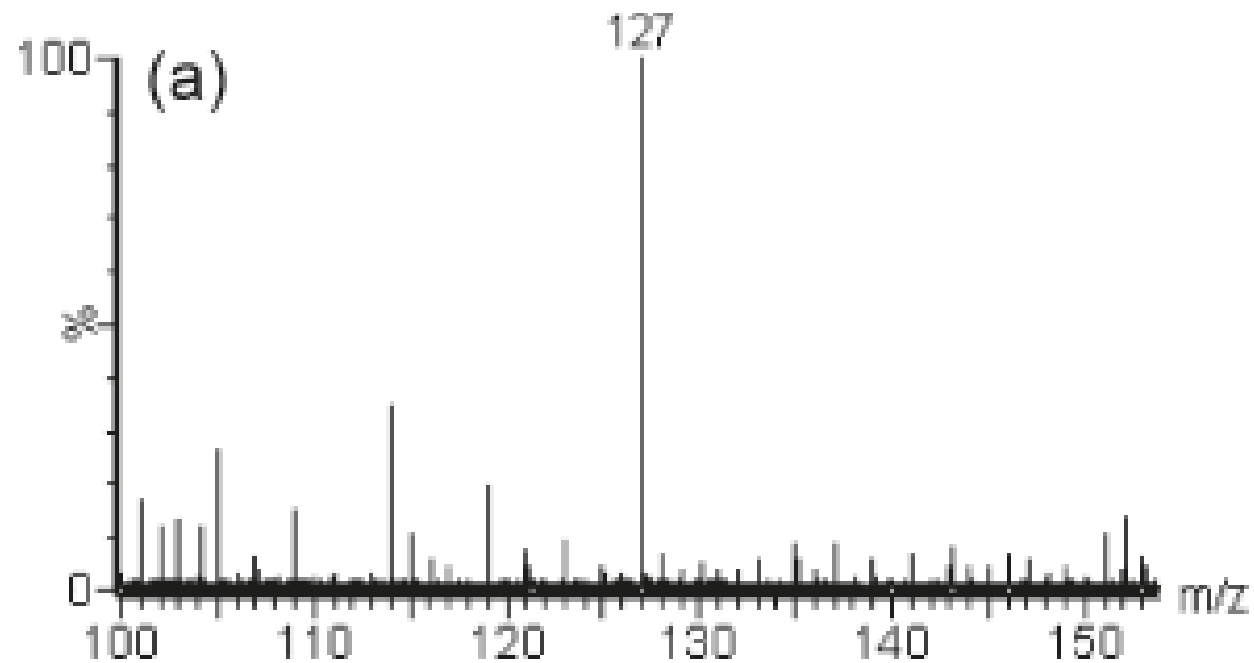
Completely digested  
cytochrome C

11 peptides identified  
covering 73% of the amino  
acid sequence of protein



(a) Total ion chromatogram (TIC) obtained for the incompletely digested cytochrome C, (b and c) extracted ion chromatograms of representative mass peaks of undigested protein (m/z 1224) and the tryptic peptide (m/z 634), respectively. (d and e) Mass spectra obtained for the period of T1 in part b and T2 in part c, respectively. (f) Mass spectra obtained for the incompletely digested cytochrome C using nano-ESI. Mass peaks of undigested cytochrome C are labeled with an \*.

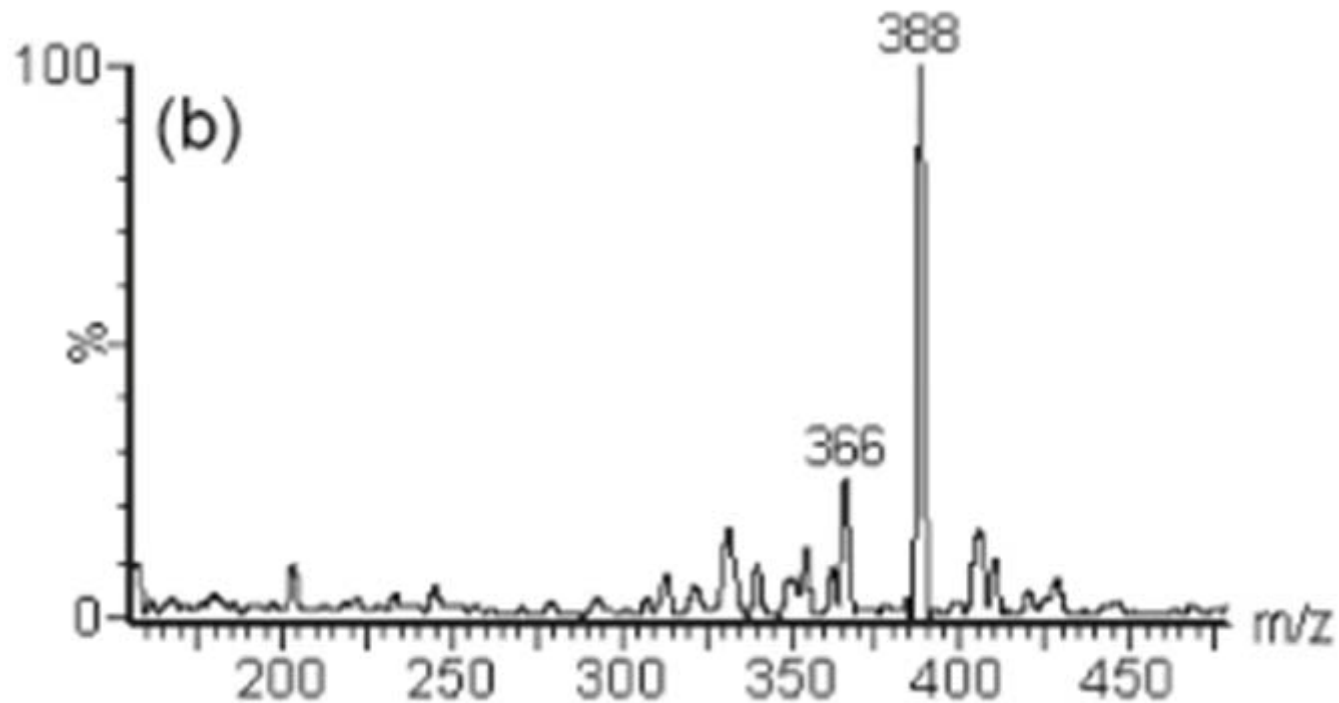
## Analysis of raw biological liquid samples:



Slurry of MC in urine (5  $\mu\text{L}$ ) is analyzed.

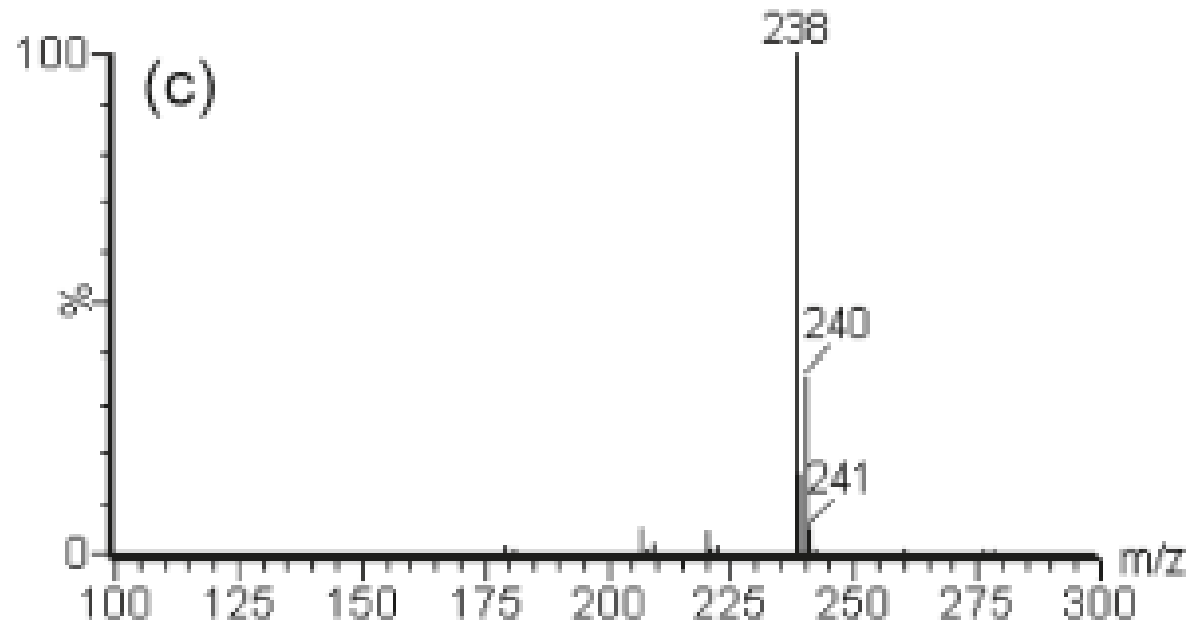
Melamine cyanurate (MC), an insoluble complex between melamine and cyanuric acid and is the cause of fatal kidney stones.

## Analysis of powder samples:



Wooden tip was prewetted with MeOH/H<sub>2</sub>O (1/1) containing 0.1% formic acid on the tip-end. Scraped with a powder of amoxicillin, a commonly used  $\beta$ -lactam antibiotic. 5  $\mu$ L of driving solvent (MeOH/H<sub>2</sub>O (1/1) containing 0.1% formic acid) was loaded onto the tip.

## Applications in forensic analysis:



Concrete floor was spiked with ketamine, a commonly abused recreational drug. Prewetted wooden tip was inserted into a crack on concrete and scraped in a circular motion until a layer of powder was adhered to the tip end. Driving solvent was added.

# SUMMARY AND CONCLUSION

Electrospray ionization using a wooden tip has been demonstrated.

The hydrophilic and porous nature of wood allows effective adhesion of sample solution and thus acquisition of durable ion signals.

The slim and hard properties of wooden tips also allow sampling from specific locations, e.g., corners and small openings.

The ionization of the new method is very gentle and enables observation of native proteins, noncovalent complexes (myoglobin), and organometallic complexes (iron(II) acetylacetonate).

A mixture of a protein and some peptides, could be separately detected with this new method.

This method was applicable for direct analysis of raw biological samples and powder samples, indicating the potential applications in clinical and forensic analysis.

The successful use of wood as sampling and ionization media in ESI not only simplifies ESI analysis but also brings us a new vision to the ESI technique.

# **FUTURE POSSIBILITIES**

Protein protected clusters can be analyzed.

Cluster from gel or biological slurry materials can be analyzed.

**THANK YOU**