A New Mass Spectrometry Analytical Method Assisted by Laser Desorption

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Mass Spectrometry (MS) analysis method presented in this paper consists of YagNd laser desorption of the analyte molecules and their ionization by internal ionization mass spectrometry. The MS analysis on ibuprofen, a drug which is on the list of doping substances, evidenced that using the proposed method, molecular fragments responsible for doping action can be identify.

1. Introduction

Mass spectrometry (MS) has become a powerful and widerange technique in analytical and bioanalytical investigations. This overwhelming success and its broadness has resulted mainly from the unmatched abilities of MS to detect, count, and characterize atoms and molecules of many types, compositions, and sizes. The combination of high sensitivity, selectivity, and speed ("The 3 S trademark of MS") has long been a major advantage of MS. More recently, MS has also become very general with regard to types of molecules and mixtures, being able to handle not only relatively small and thermally stable organic molecules but also nearly all types of biomolecules, organic and inorganic salts, organometallic complexes, supramolecular entities and biological species. To deal with such great variety of atoms and molecules, matrices and mixtures, MS needs to promote efficient ionization to generate diagnostic ions that can be transferred to the high vacuum environment of mass spectrometers where they are characterized and counted. Major difficulties occurred in the process of transferring the analyte molecules from their "real world" ambient environment, in which target molecules are normally found often in condensed forms together with matrices and, in complex mixtures, into the clean but quite "inhospitable" high vacuum MS environment in which traditional MS ionization techniques, for example electron ionization (EI), chemical ionization (CI), and secondary ion MS (SIMS) had normally to be performed on pure gaseous molecules.

In this paper, we present a new system interface coupled to mass spectrometer able to analyse the sensitive samples contaminated with drug traces. The molecules are desorbed with a pulsed YagNd laser, than directed by a stream of argon into the slit of the MS set at internal ionization where the generated and fragment ions are detected.

2. Results and Discussions

The experimental set-up is presented in Figure.1.

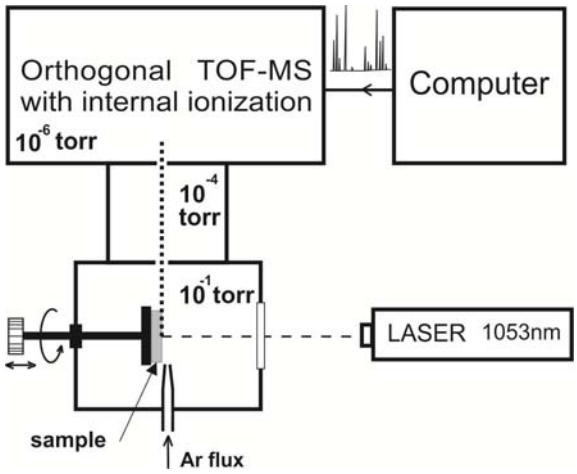

Figure 1 Experimental set up

The laser desorption, the first step of our analytical method, has the advantage of reducing a possible thermal decomposition of sample for analysis, allows rapid analysis and uses relatively simple equipment. In order to avoid the rapid heating of the sample, we used a pulsed laser and an optical system designed quickly scans the laser radiation on the surface of the analyte.

In this paper we evidenced the desorption process on powdered samples (ibuprofen) using a pulsed YagNd laser with the wavelength 1053 nm, 0.01-1kHz with energy ≥250μJ/puls, the pulse duration 7±3 ns and the beam diameter 2.3±0.5mm. The laser beam is directed on the sample surface in the interface cell through a quartz window. The sample, ibuprofen powder, is placed on the end of a rod positioned into the interface in front of the laser entrance window. The interface cell attached to mass spectrometer has its own vacuum system which allows the pressure control 10^{-1} Torr inside the cell. As it can be seen in the Figure 1, the Argon flux directed on the entrance slit of the MS Spectrometer

train the desorbed molecules into the Spectrometer where there are ionized by the inner electron gun and detected.

We tested our method and corresponding interface cell on Ibuprofen ($C_{13}H_{18}O_2$), Figure 2, a drug which is on the list of banned doping athletes.

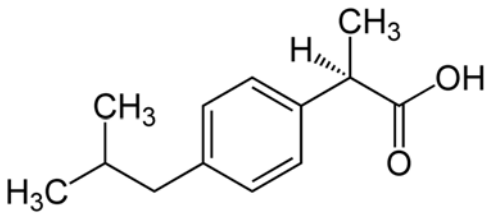

Figure 2 Ibuprofen chemical structures

Investigation of the structure of ibuprofen is important because it allows the identification of active and poor groups in charge of medical activity of ibuprofen. The mass spectrum recorded by the method proposed by us, allowed the identification of the correct pathway fragmentation of this product. The obtained MS spectrum of ibuprofen using our new method is presented in Figure 3. Our results were in good agreement with the results obtained in [2]. The experiment, simultaneous irradiation with argon flow (35 Sl/m) training of the sample, lasts 30 seconds.

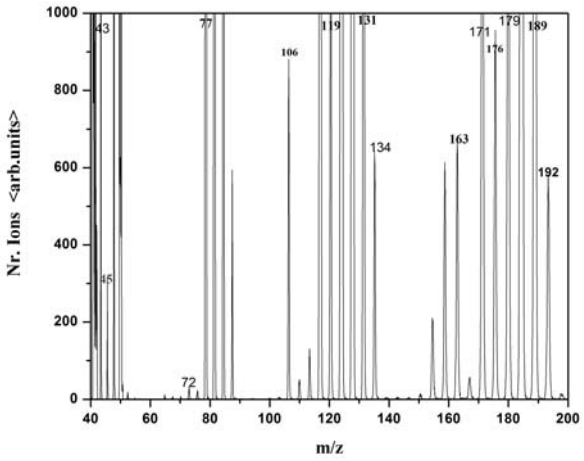

Figure 3 MS spectrum of Ibuprofen with an analytical method assisted by laser desorption

MS spectrum (Figure 3) suggests possible fragmentation schemes, Figure 4, of ibuprofen desorbed by YagNd laser and ionized with the internal electron gun of mass spectrometer.

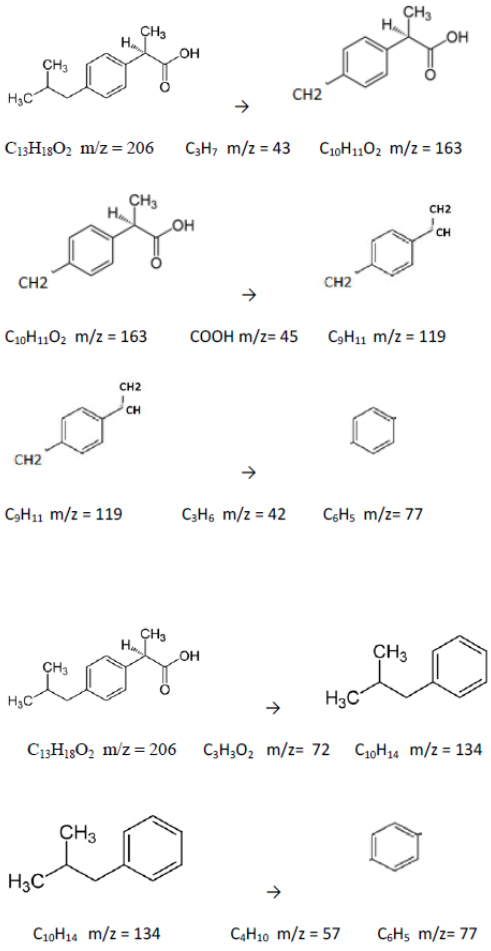

Figure 4 Fragmentation schemes of Ibuprofen

It can be seen in the Figure 4 that the first fragmentation is carried out by the loss propyl, C_3H_7 (m / z = 43) that leads to the formation of ion m / z = 163. Another ion in the spectrum is observed at m / z = 119 ion is due by breaking the group COOH m/z =45 of m / z = 163 $C_{10}H_{11}O_2$ fragment. Another fragmentation scheme involves breaking the group m/z = 72 with the formation of the ion m/z = 134. The loss of m/z= 57 of the fragment m/z= 134 leads to the formation of the ion m/z = 77.

3. Conclusions

The new proposed analytical method based on mass spectroscopy assisted by laser desorption was proved to be in good agreement with other classical methods. This technique requires relatively simple equipment allowing rapid analysis and it has the advantage of reducing a possible thermal decomposition of sample for analysis.

4. Acknowledgements

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References

[1] E. Hoffmann, V. Stroobant V, *Mass spectrometry: principles and applications,* 3rd edn. Wiley, (2007) London

[2] Mohamed A. Zayed, M. F. Hawash, M. A. Fahmey, Ali M. M. El-Gizouli, J Therm Anal Calorim (2012) 108:315–322