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Analysis of illicit drugs by direct ablation of solid samples

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Analysis of illicit drugs arises as an important field of work given the high social impacts presented by drugs in the modern society. Direct laser ablation of solid compounds allows their analysis without sampling or preparation procedures. For that purpose, an experimental set-up that combines laser ablation with time-of-flight mass spectrometry has been constructed very recently to perform studies on the mass spectra of such drugs as 3,4-methylenedioxy-*N*-methylamphetamine, commonly known as MDMA or ecstasy. Analysis of the observed fragmentation pattern in mass spectra may elucidate the ablation-induced photofragmentation phenomena produced, which differ from those previously observed with conventional ionization methods.

Keywords: ecstasy, laser ablation, mass spectrometry, drugs, sample analysis

Introduction

Direct chemical analysis of solid samples by mass spectrometry (MS) without chemical pretreatment can offer advantages over conventional dissolution techniques used in the analysis of real samples, such as high-pressure liquid chromatography and gas chromatography coupled with MS.[1,2] Elimination of chemical solvents and wastes, reduced sample handling, and short analysis times are some of the benefits offered by direct solid-sampling techniques, not to mention that it may provide an analysis of all the components of the sample without any previous separation. Laser ablation has raised considerable interest because of its proven applications in solid-sample analysis and consequently different analytical techniques in combination with laser ablation have been developed during the past few decades. Laser-induced breakdown spectroscopy[3,4] and laser ablation optical/mass spectrometry with an inductively coupled plasma[5–10] appear to be amongst the most powerful analytical techniques for the nearly nondestructive determination of elements. However, with the growing importance of biomedical and forensic investigations in organic analysis, the emphasis has been shifting towards detection of ever larger molecules. Hence, devoted laser-based MS techniques, such as laser microprobe mass analysis[11–14] and laser desorption/ionization mass spectrometry (LDI-MS)[15–17] have been developed. Among all the LDI systems, matrix-assisted laser desorption/ionization (MALDI)[18–20] is the most extensively used because of its capacity to analyze samples of up to 1.5 million Daltons.[21] However, matrix selection presents itself as a crucial step since matrices are normally too specific and, furthermore, the matrix-to-analyte molar ratio is difficult to adjust correctly.[22,23] Alternative techniques for LDI, such as using metals,[17] surfaces,[24] nanoparticles[25] and polymers,[26] have been developed in order to circumvent the problems with sample preparation in MALDI.

During the past decade, laser ablation has been successfully combined with Fourier transform microwave techniques to bring thermally unstable biomolecules into the gas phase and reveal their most stable structures. Narrow-band laser ablation molecular beam Fourier transform microwave[27]

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and broadband chirped pulse Fourier transform microwave[28] techniques have overcome the drawback of vaporizing solid samples, opening a new window to high-resolution rotational studies. In so doing, the conformational behavior of relevant building blocks such as amino acids,[29] sugars[30] and nucleic acid bases,[31] as well as the drugs aspirin[32] and paracetamol,[33] could be unveiled.

On the basis of previous experimental set-ups developed for identifying metallic contaminants[34] and taking advantage of our long experience on laser ablation techniques, an experimental set-up that combines laser ablation with time-of-flight mass spectrometry (LA-TOF-MS) has been developed to be dedicated to analyze organic compounds. The instrument configuration is described in the following section and preliminary results on several drugs (such as aspirin and paracetamol) and seized samples, such as the illicit drug MDMA (3,4-methylenedioxy-*N*-methylamphetamine, also known as ecstasy) are reported.

Materials and methods

Experimental set-up

The LA-TOF-MS experimental set-up has been developed in-house by using a combination of commercial components. Figure 1 shows a diagram of the overall system. The ionization chamber is a multiport stainless-steel vacuum cavity in which samples are introduced through port 1. The samples are presented in the shape of a pill, with a diameter of 8 mm and length of 5 mm, and are linked to the holder via a heat shrink tube. A gate valve is used to avoid vacuum losses each time a new sample is inserted. The horizontal position of the sample can be adjusted to obtain the best signal. Samples are vertically fixed at the halfway point between the TOF extractor and the repeller plates. Port 2 is coupled to the TOF tube in such a way that its extractor and repeller plates are located in the middle of the chamber. The TOF tube employed is a Jordan-type tube 1 m long that can operate in the reflectron mode (RM Jordan, model D-850). Several voltage-adjustable plates along the tube are used to optimize the signal of the samples. All of these work in a continuous mode with the exception of the repeller and extractor plates, which have been modified by two high-voltage rapid switches in order to pulse them. The laser beam is introduced inside the ionization chamber though a glass window placed in port 3. This beam is aligned by two external mirrors in such a way that it is equally spaced between the extractor and repeller plates; as such, the laser ablation/ionization is produced perpendicularly to the sample. The laser employed is a neodymium:yttrium aluminum garnet (Quantel Brilliant, model C07.BR) in the third harmonic (λ = 355 nm) with pulse width ~5 ns. Its power is adjusted to modify the time delay between the flash lamp and the Q-S pulse. A single lens (Melles Griot), with a focal distance of 750 mm, which is placed between the above-mentioned two mirrors, is employed to focus the laser beam onto the sample. The distance from the lens to the target is tuned by employing a translation stage, which allows the beam spot area to be to modified in order to obtain a stable signal. The laser spot

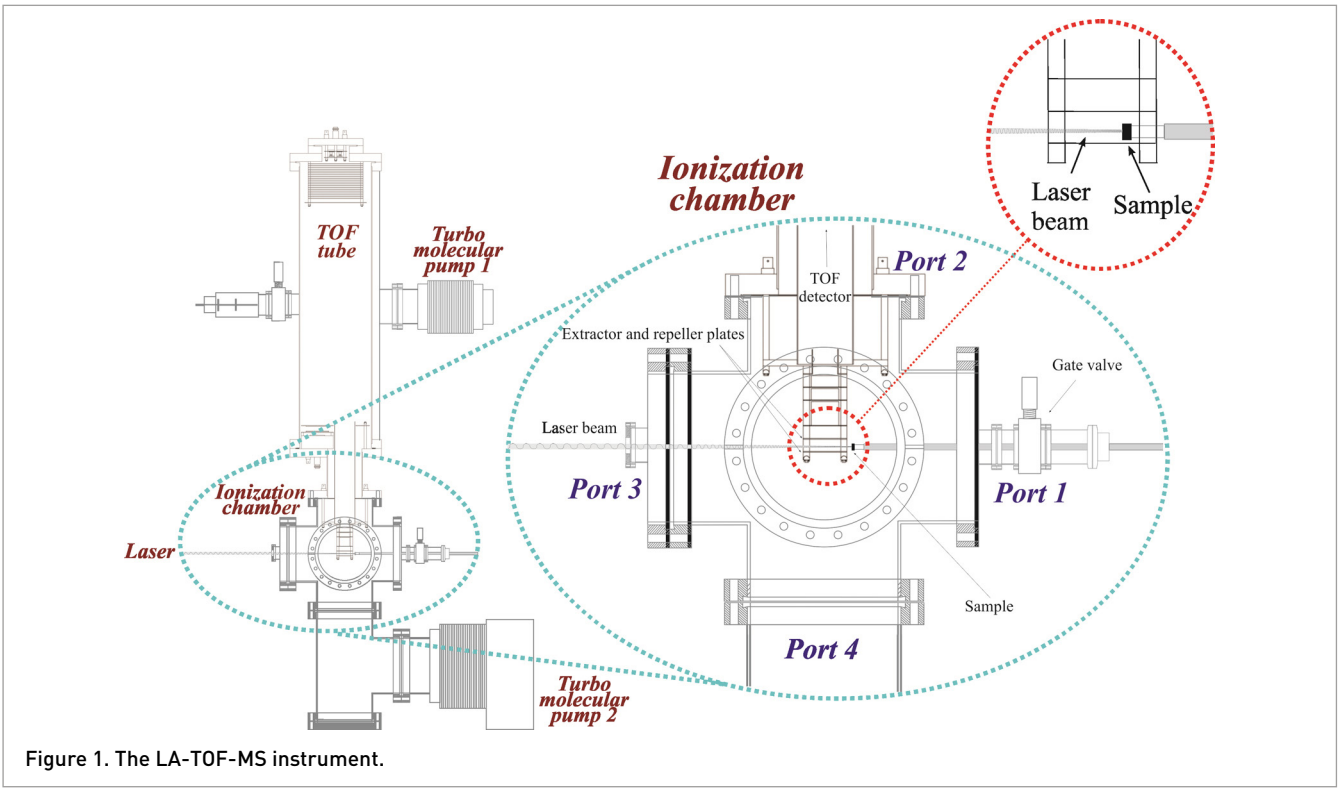

Figure 1. The LA-TOF-MS instrument.

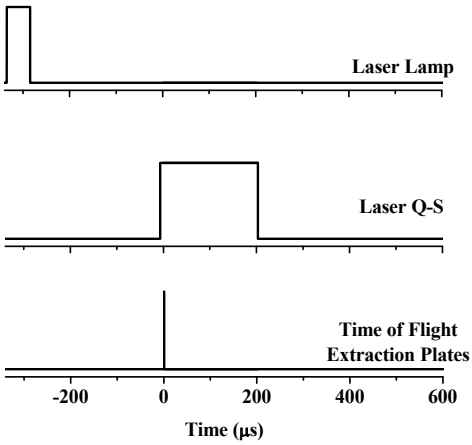

Figure 2. Operating sequence of the LA-TOF-MS controlled by a pulse-delay generator.

size is around 0.6 cm^2. Two turbo molecular pumps (Leybold, model TDL RS 458 and TURBOVAC, model 361) connected though port 4 and in the TOF tube are used to maintain the ultrahigh vacuum required for the experiment. The ionization chamber is generally at 10^{-7} Torr while the reflectron TOF is at 10^{-8} Torr.

The experimental sequence (Figure 2) is controlled by a commercial delay generator (Stanford Research Systems, model DG-645) working at a repetition rate of 10 Hz. Both the flash lamp and the Q-switch of the laser are externally triggered by the delay generator, the Q-switch being delayed from the flash lamp by around 300 μs; this period changes as a function of the energy that is required for the sample to be ionized. A few microseconds after the Q-switch, the extractor and repeller plates are pulsed during a period that may range from less than a microsecond to 20 μs. Delays and pulsed widths are tuned to accomplish the maximum signal of the interested ions. The most common experimental timings are summarized in Table 1. The output signal of the extraction plates is used to trigger the oscilloscope [Agilent model 5464D, 2 GS s^{-1} (GS, gigasample)], which digitalized the signal coming from the multichannel plate of the TOF tube. Afterwards, the data are sent to a computer in which the analysis and graphing is performed. The ions time of flight is converted to mass/charge ratio based on the calibrations made with some metal samples (see Figure 3).

Sample preparation

Samples used for the analysis, such as aspirin [melting point (m.p.) 137°C) or paracetamol (m.p. 171°C), were purchased from Sigma Aldrich with the exception of MDMA (m.p. 100–110°C), which is a street sample (not pure) obtained from a seizure by the Valladolid Division of the Spanish Police Department. This seized sample came as a fine powder taken from the street. The samples were used without further purification. They were ground and then introduced into a cast designed in-house and pressed into a hydraulic press at 50 bar in order to form pills

Table 1. Summary of the operating parameters of the LA-TOF-MS system.

Laser	
Wavelength	355 nm
Pulse width	5 ns
Energy per pulse	0.5–15 mJ
Rep rate	10 Hz
Spot size	0.6 cm^2
Time of flight	
Pressure	~10^{-7} Torr
Extraction plate	~2800 V
Repelling plate	~3250 V
Reflection plate 1	~1800 V
Reflection plate 2	~4000 V
Deflection plates	~0 V
Detection plate	~−4000 V
Pulse delay generator	
Delay flash lamps/Q-switch	300–350 μs
Delay Q-switch/extraction plates	1–15 μs
Pulse width of extraction plates	0.5–5 μs

8 mm in diameter and 5 mm in length. This procedure has been extensively described in our group reports.[27–33] The metal samples (Ag and Cu) were modeled with the same dimensions as the organic pills in our laboratory.

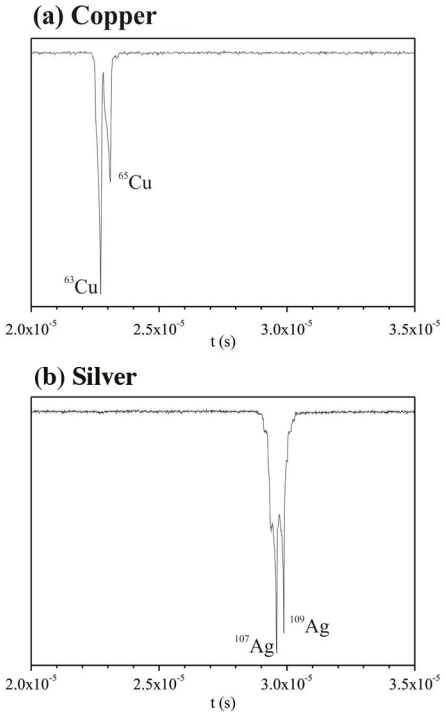

Figure 3. Mass spectra of some metals obtained from the LA-TOF-MS instrument.

Results and discussion

Prior to the analysis of the illicit drug MDMA, several organic compounds of similar physical characteristics (solids with comparable melting points) have been proved by LA-TOF-MS. The pharmacological species paracetamol and aspirin were employed to optimize the experimental conditions and their mass spectra were successfully obtained using this technique (see Figure 4). Both substances exhibit similar fragmentation patterns to those obtained by employing electron impact (EI), a more common ionization source.[35] However, the intensity ratio of the fragments is slightly different. In the case of paracetamol, the cleavage between the carbonyl and amino groups [indicated in Figure 4(a)] has diminished drastically, leading to a major proportion of the parent ion (151 u) being observed. Likewise, for aspirin, the ratio between the different possible cleavages changed [see Figure 4(b)]. For EI ionization, the most abundant fragment is by far that corresponding to 120 u, with minimal proportions of 163 u and 138 u, the latter being slightly higher. In contrast, employing LA-TOF-MS, the 120 u peak decreased its intensity and, moreover, the proportion between 163 u and 138 u is inverted; in fact, the peak corresponding to 138 u does not appear in our mass spectrum.

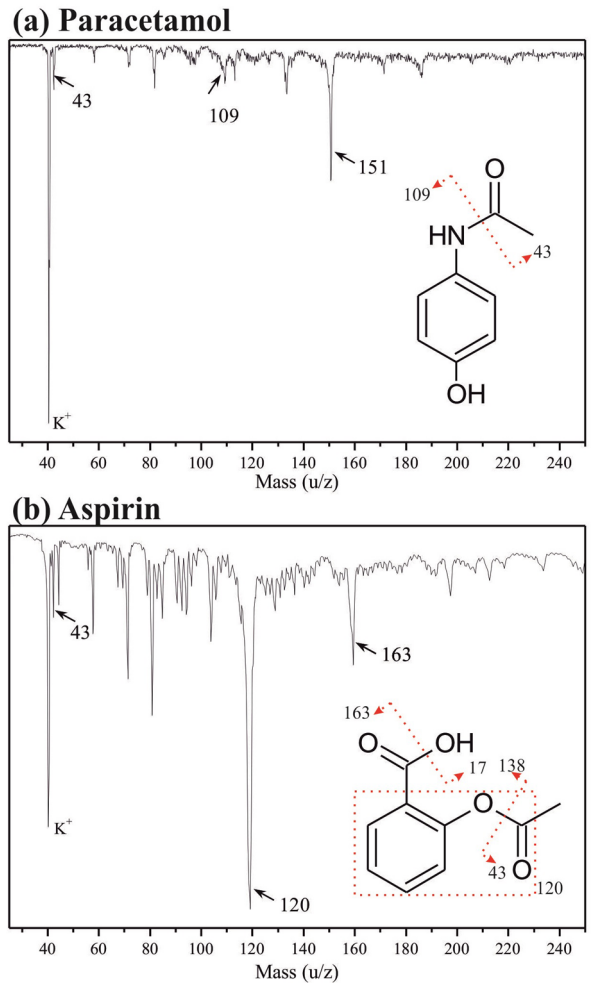

Figure 4. Mass spectra of paracetamol (151 u) and aspirin (180 u) obtained from the LA-TOF-MS instrument.

In light of the results obtained in these initial tests, the analysis of the seized sample MDMA was carried out. This analysis was executed under the same conditions as for previous compounds, with the exception of the laser power effects over the sample which were analyzed in order to optimize them. Figure 5 shows several spectra obtained at different fluencies. There, it is remarkable that the value of the energy per pulse might drastically change the aspect of the mass spectrum. At low fluencies, the first signal registered corresponds to a mass/charge of 23 and dominates the mass spectrum even at higher fluencies. This peak presumably corresponds to the Na^+, which is present in most of the commercial organic compounds. Rising in energy, signals of heavier ions become appreciable, including the molecular peak at 193 u, corresponding to the parent $[MDMA]^+$ ion. However, if the energy exceeds an optimum value, peaks that correspond to a much higher fragmentation saturate the spectrum (signals around 12 u and 24 u) while the $[MDMA]^+$ disappears. On reaching this energy range, the laser power is enough to break most of the bonds of the organic molecules that are present in the ablation plume. Thus, for the MDMA analysis, the optimum energy per pulse found was around 5.7 mJ $pulse^{-1}$, which is close to the energy employed for the other organic samples analyzed.

In the MDMA spectrum at 5.7 mJ $pulse^{-1}$ [Figure 5(b)], besides the 193 u fragment corresponding to the parent ion ($[MDMA]^+$), several ions at *m/z* equal to 30, 42, 58, 122, 105, 135 and 163 u can also be attributed to fragments from MDMA, according to mass spectrum libraries.[35] Between the three main possible cleavage sites for the ecstasy molecule [Figure 5(c)], β- and γ-cleavages are given at a higher proportion according to the almost equal intensity of the fragments, *m/z* = 135 and 163, representative of these two cleavages, respectively. Both signals are about three times stronger than those of the parent ions, which gives us an idea of the fragmentation degree of MDMA under these experimental conditions.

Comparing this LA-TOF-MS spectrum with those obtained from more conventional ionization methods, there are clear discrepancies in the relative intensities of the fragments that might indicate differences in the fragmentation procedure. In the case of EI ionization, β-cleavage [Figure 5(c)] dominates the mass spectrum, with negligible intensities of either of the other fragments or the parent ion. This β-cleavage also has a higher relevance related to α and γ in MALDI experiments,[36] although, in this case, the photofragmentation degree is minimal; the intensities of the fragment signals are almost exiguous in the spectrum. In contrast to these two ionization methods (EI and MALDI), electrospray ionization (ESI) produces a rupture via γ-cleavage[36] instead of the β-cleavage. On the other hand, as mentioned before, both γ- and β-cleavages are produced in almost equal amounts when laser ablation is used to ionize the samples. Thus, laser ablation fragmentation is not produced in exactly the same way as any of the others, being more of a combination of cleavages.

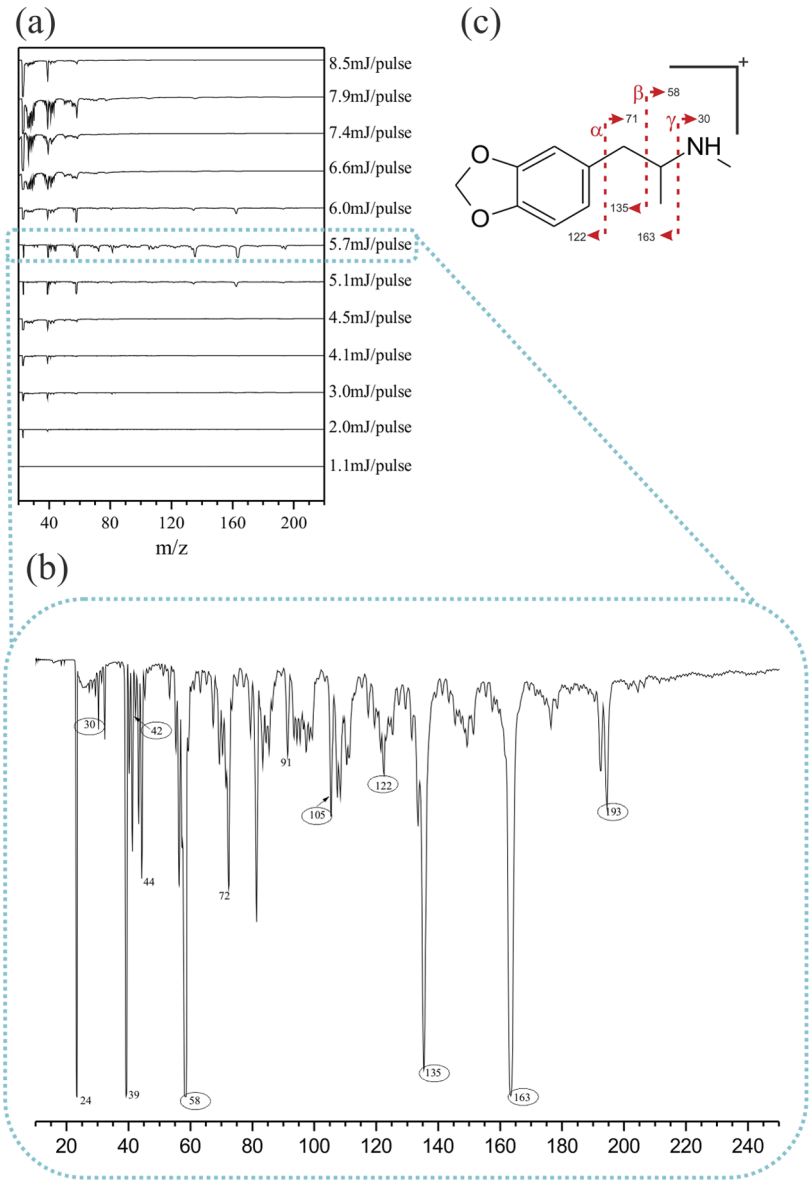

Figure 5. (a) Mass spectra of MDMA at different fluencies. (b) Mass spectrum of MDMA at 5.7 mJ pulse^{-1} amplified. (c) α-, β- and γ-cleavages of MDMA.

Deeper insight into the MDMA spectrum reveals that signals with a relative high intensity non-assignable to this illicit drug can be distinguished. One should take into account that the sample analyzed was not a pure sample (estimated purity 70%), but obtained from a seizure made by the Spanish police. Therefore, the presence of other analytes should be expected. By screening mass spectra libraries,[35] it was found that several peaks are consistent with the existence of *N*-ethylamphetamine (Ph–CH_2–CH(CH)–NH–CH_2–CH_3), sometimes present together with MDMA as a stimulant. This possible assignment is based on the signals at 72 u and 91 u and at 44 u and 119 u that might correspond to the pair of ions produced by the break of ethylamphetamine through β- and δ-cleavages, respectively. In this case, both types of cleavage have almost the same relevance, similar to those in MDMA. However, in the latter, the β-type is slightly more intense. The signal at 163 u, assigned initially to a γ fragment of MDMA, could also have increased its contribution because of the parent peak of *N*-ethylamphetamine, shedding some light on the intensity discrepancies between the two peaks produced by γ-cleavage (31 u and 163 u). Besides these two analytes, no other signals assignable to any other species could be identified in the spectrum.

Conclusions

To the best of our knowledge, this is the first report of the utilization of conventional laser ablation/ionization TOF-MS spectrometry that aims to detect the presence of illicit drugs in real

samples. Our results show the capacity of this technique as a fast diagnostic method for all of the components of a sample with a reduced sample processing, which constitutes a major advantage and serves as a foundation for future investigations on the implementation of laser ablation/ionization TOF-MS spectrometry for the detection of illicit drugs. Moreover, it was found that laser ablation produces different fragmentation patterns when compared to most conventional ionization methods (ESI, EI and MALDI). Hence, more work will be necessary to optimize the laser ablation conditions, for instance, by using picosecond laser pulses.

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References

1. N. Pizarro, J. Ortuño, M. Farré, C. Hernández-López, M. Pujadas, A. Llebaria, J. Joglar, P. N. Roset, M. Mas, J. Segura, J. Camí and R. de la Torre, "Determination of MDMA and its metabolites in blood and urine by gas chromatography-mass spectrometry and analysis of enantiomers by capillary electrophoresis", *J. Anal. Toxicol.* **26(3),** 157 (2002). doi: http://dx.doi.org/10.1093/jat/26.3.157
2. A. Namera, A. Nakamoto, T. Saito and M. Nagao, "Colorimetric detection and chromatographic analyses of designer drugs in biological materials: a comprehensive review", *Forensic Toxicol.* **29(1),** 1 (2011). doi: http://dx.doi.org/10.1007/s11419-010-0107-9
3. A.W. Miziolek, V. Palleschi and I. Schechter, *Laser Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications*. Cambridge University Press, New York (2006).
4. J.P. Singh and S.N. Thakur, *Laser Induced Breakdown Spectroscopy*. Elsevier, Amsterdam (2007).
5. D. Günther, S.E. Jackson and H.P. Longerich, "Laser ablation and arc/spark solid sample introduction into inductively coupled plasma mass spectrometers", *Spectrochim. Acta B* **54(3–4),** 381 (1999). doi: http://dx.doi.org/10.1016/S0584-8547(99)00011-7
6. S.F. Durrant, "Laser ablation inductively coupled plasma mass spectrometry: achievements, problems, prospects", *J. Anal. At. Spectrom.* **14(9),** 1385 (1999). doi: http://dx.doi.org/10.1039/a901765h
7. J.D. Winefordner, I.B. Gornushkin, D. Pappas, O.I. Matveev and B.W. Smith, "Novel uses of lasers in atomic spectroscopy", *J. Anal. At. Spectrom.* **15(9),** 1161 (2000). doi: http://dx.doi.org/10.1039/a910219l
8. D. Günther, I. Horn and B. Hattendorf, "Recent trends and developments in laser ablation–ICP–mass spectrometry", *Fresenius J. Anal. Chem.* **368(1),** 4 (2000). doi: http://dx.doi.org/10.1007/s002160000495
9. R.E. Russo, X. Mao and O.V. Borisov, "Laser ablation sampling", *Trends Anal. Chem.* **17(8–9)**, 461 (1998). doi: http://dx.doi.org/10.1016/S0165-9936(98)00047-8
10. R.E. Russo, X.L. Mao, O.V. Borisov and H.C. Liu, in *Encyclopedia of Analytical Chemistry*, Ed by R.A. Meyers. Wiley, Chichester, p. 9485 (2000).
11. F. Hillenkamp, E. UnsoLd, R. Kaufmann and R. Nitsche, "Laser microprobe mass analysis of organic materials", *Nature* **256(5513),** 119 (1975). doi: http://dx.doi.org/10.1038/256119a0
12. L. Van Vaeck, J. Bennett, P. Van Epsen, E. Schweikert, R. Gijbels, F. Adams and W. Lauwers, "Structural characterization of organic molecules by negative ions in laser microprobe mass spectrometry", *Org. Mass Spectrom.* **24(9),** 782 (1989). doi: http://dx.doi.org/10.1002/oms.1210240912
13. L. Van Vaeck, H. Struyf, W. Van Roy and F. Adams, "Organic and inorganic analysis with laser microprobe mass spectrometry. Part I: Instrumentation and methodology", *Mass Spectrom. Rev.* **13(3),** 189 (1994). doi: http://dx.doi.org/10.1002/mas.1280130302
14. L. Van Vaeck, H. Struyf, W. Van Roy and F. Adams, "Organic and inorganic analysis with laser microprobe mass spectrometry. Part II: Applications", *Mass Spectrom. Rev.* **13(3),** 209 (1994). doi: http://dx.doi.org/10.1002/mas.1280130303
15. M.A. Posthumus, P.G. Kistemaker, H.L.C. Meuzelaar and M.C. Ten Noever de Brauw, "Laser desorption–mass spectrometry of polar nonvolatile bio-organic molecules", *Anal. Chem.* **50(7),** 985 (1978). doi: http://dx.doi.org/10.1021/ac50029a040
16. R.J. Levis, "Laser desorption and ejection of biomolecules from the condensed phase into the gas phase", *Ann. Rev. Phys. Chem.* **45(1),** 483 (1994). doi: http://dx.doi.org/10.1146/annurev.pc.45.100194.002411
17. E.P.C. Lai, S. Owega and R. Kulczycki, "Time-of-flight mass spectrometry of bioorganic molecules by laser ablation of silver thin film substrates and particles", *J. Mass Spectrom.* **33(6),** 554 (1998). doi: http://dx.doi.org/10.1002/(SICI)1096-9888(199806)33:6<554::AID-JMS661>3.0.CO;2-2
18. K. Tanaka, H. Waki, Y. Ido, S. Akita, Y. Yoshida, T. Yoshida and T. Matsuo, "Protein and polymer analyses up to *m/z* 100000 by laser ionization time-of-flight mass spectrometry", *Rapid Commun. Mass Spectrom.* **2(8),** 151 (1988). doi: http://dx.doi.org/10.1002/rcm.1290020802
19. M. Karas and F. Hillenkamp, "Laser desorption ionization of proteins with molecular masses exceeding

10,000 Daltons", *Anal. Chem.* **60(20),** 2299 (1988). doi: http://dx.doi.org/10.1021/ac00171a028

20. K. Dreisewerd, "The desorption process in MALDI", *Chem. Rev.* **103(2),** 395 (2003). doi: http://dx.doi.org/10.1021/cr010375i

21. D.C. Schriemer and L. Li, "Detection of high molecular weight narrow polydisperse polymers up to 1.5 million Daltons by MALDI mass spectrometry", *Anal. Chem.* **68(17),** 2721 (1996). doi: http://dx.doi.org/10.1021/ac960442m

22. E.T.P. Sze, T.W.D. Chan and G. Wang, "Formulation of matrix solutions for use in matrix-assisted laser desorption/ionization of biomolecules", *J. Am. Soc. Mass Spectrom.* **9(2),** 166 (1998). doi: http://dx.doi.org/10.1016/S1044-0305(97)00237-7

23. M. Vestling Martha, in *Time-of-Flight Mass Spectrometry* Vol. 549, Ed. by R.J. Cotter. American Chemical Society, Washington, p. 211 (1993).

24. K.P. Law and J. Larkin, "Recent advances in SALDI-MS techniques and their chemical and bioanalytical applications", *Anal. Bioanal. Chem.* **399(8),** 2597 (2011). doi: http://dx.doi.org/10.1007/s00216-010-4063-3

25. J. Niziol, W. Rode, Z. Zieliński and T. Ruman, "Matrix-free laser desorption–ionization with silver nanoparticle-enhanced steel targets", *Int. J. Mass Spectrom.* **335,** 22 (2013). doi: http://dx.doi.org/10.1016/j.ijms.2012.10.009

26. A. Woldegiorgis, F. v. Kieseritzky, E. Dahlstedt, J. Hellberg, T. Brinck and J. Roeraade, "Polymer-assisted laser desorption/ionization analysis of small molecular weight compounds", *Rapid Commun. Mass Spectrom.* **18(8),** 841 (2004). doi: http://dx.doi.org/10.1002/rcm.1412

27. J.L. Alonso, C. Perez, M.E. Sanz, J.C. Lopez and S. Blanco, "Seven conformers of L-threonine in the gas phase: a LA-MB-FTMW study", *Phys. Chem. Chem. Phys.* **11(4),** 617 (2009). doi: http://dx.doi.org/10.1039/b810940k

28. S. Mata, I. Peña, C. Cabezas, J.C. López and J.L. Alonso, "A broadband Fourier-transform microwave spectrometer with laser ablation source: the rotational spectrum of nicotinic acid", *J. Mol. Spectrosc.* **280,** 91 (2012). doi: http://dx.doi.org/10.1016/j.jms.2012.08.004

29. C. Bermúdez, S. Mata, C. Cabezas and J.L. Alonso, "Tautomerism in neutral histidine", *Angew. Chem. Int. Ed.* **53(41),** 11015 (2014). doi: http://dx.doi.org/10.1002/anie.201405347.

30. J.L. Alonso, M.A. Lozoya, I. Peña, J.C. Lopez, C. Cabezas, S. Mata and S. Blanco, "The conformational behaviour of free D-glucose-at last", *Chem. Sci.* **5(2),** 515 (2014). doi: http://dx.doi.org/10.1039/c3sc52559g

31. J.L. Alonso, V. Vaquero, I. Peña, J.C. López, S. Mata and W. Caminati, "All five forms of cytosine revealed in the gas phase", *Angew. Chem.* **48,** 5934 (2013). doi: http://dx.doi.org/10.1002/ange.201207744

32. C. Cabezas, J.L. Alonso, J.C. López and S. Mata, "Unveiling the shape of aspirin in the gas phase", *Angew. Chem. Int. Ed.* **51(6),** 1375 (2012). doi: http://dx.doi.org/10.1002/anie.201106621

33. M. Varela, C. Cabezas, J.C. López and J.L. Alonso, "Rotational spectrum of paracetamol", *J. Phys. Chem. A* **117(50),** 13275 (2013). doi: http://dx.doi.org/10.1021/jp404581z

34. R.E. Russo, G.L. Klunder, P. Grant and B.D. Andresen, "Laser ablation ion-storage time-of-flight mass spectrometry", *Appl. Phys. A* **69(1),** S895 (1999). doi: http://dx.doi.org/10.1007/s003390051554

35. NIST Mass Spec Data Center and S. E. Stein, in *Nist Chemistry WebBook*, Ed. P.J. Linstrom and W.G. Mallard. National Institute of Standards and Technology, Gaithersburg (accessed 2015). http://www.webbook.nist.gov/chemistry/

36. B.-H. Chen, J.-T. Liu, W.-X. Chen, H.-M. Chen and C.-H. Lin, "A general approach to the screening and confirmation of tryptamines and phenethylamines by mass spectral fragmentation", *Talanta* **74(4),** 512 (2008). doi: http://dx.doi.org/10.1016/j.talanta.2007.06.012