

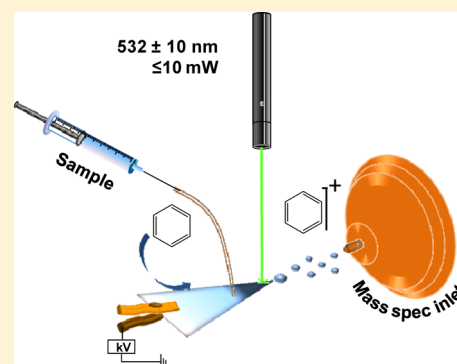
Detection of Hydrocarbons by Laser Assisted Paper Spray Ionization Mass Spectrometry (LAPSI MS)

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Supporting Information

ABSTRACT: Here we introduce a new ambient ionization technique named laser assisted paper spray ionization mass spectrometry (LAPSI MS). In it, a 532 ± 10 nm, ≤ 10 mW laser pointer was shone on a triangularly cut paper along with high voltage, to effect ionization. The analyte solution was continuously pushed through a fused silica capillary, using a syringe pump, at a preferred infusion rate. LAPSI MS promises enhanced ionization with high signal intensity of polycyclic aromatic hydrocarbons (PAHs), which are normally not ionizable with similar ionization methods involving solvent sprays. LAPSI MS works both in positive and negative modes of ionization. A clear enhancement of signal intensity was visualized in the total ion chromatogram for most analytes in the presence of the laser. We speculate that the mechanism of ionization is field assisted photoionization. The field-induced distortion of the potential well can be large in paper spray as the fibers comprising the paper are separated at tens of nanometers apart, and consequently, the analyte molecules are subjected to very large electric fields of the order of 10^7 Vcm⁻¹. Ionization occurs from their distorted electronic states of reduced ionization energy, using the laser. Negative ion detection is also demonstrated, occurring due to the capture of produced photoelectrons. LAPSI MS can be used for monitoring in situ photoassisted reactions like the decarboxylation of mercaptobenzoic acid in the presence of gold and silver nanoparticles and the dehydrogenation reaction of 2,3-dihydro-1H-isoindole, which were chosen as examples. As an application, we have shown that paraffin oil, which is usually nonionizable by paper spray or by electrospray ionization can be efficiently detected using this technique. Impurities like mineral oils were detected easily in commercially available coconut oil, pointing the way to applications of social relevance.



Ambient ionization methods such as electrospray ionization (ESI),¹ desorption electrospray ionization (DESI),^{2–4} low temperature plasma (LTP)⁵ ionization, etc., have emerged as some of the most important directions in modern mass spectrometry. One of the important subclasses of this discipline is paper spray ionization mass spectrometry,^{6,7} which has importance in several analytical situations such as blood clot analysis,^{8,9} forensic analysis,¹⁰ food adulteration,^{11,12} monitoring catalysis reactions,^{13,14} etc. Variation of the same, such as leaf spray (LS)^{15,16} ionization, has also been useful in a number of situations. Despite important advantages, the technique has certain limitations in analyzing specific categories of analytes such as alkanes, olefins, polycyclic aromatic hydrocarbons (PAHs), etc. This stems from the fact that the electrospray technique in general is inefficient in causing ionization for certain classes of molecules. For such molecular systems, an approach to overcome this limitation is to use other stimuli complementing the electric field available in paper spray.

We show that a simple laser pointer is adequate to assist the electric field and cause measurable ion intensity for a diverse variety of analytes. This modified paper spray referred to as laser assisted paper spray ionization mass spectrometry (LAPSI MS) is introduced in this article. The paper illustrates the application of this technique for several aromatic molecules that

are not amenable for common paper spray ionization. In order to establish the field assisted photoionization process, experiments have been conducted with analytes of different ionization potentials. The experimental methodology has been applied to an important situation involving the detection of paraffin oil¹⁷ (a common example of hydrocarbons) in adulterated coconut oil. It further shows the utility of the methodology of paper spray in detecting laser-induced transformations.

MATERIALS AND METHODS

Chemicals and Sample Preparation. All the chemicals were purchased commercially and used without further purification. Benzene, naphthalene, pyrene, benzanthracene, C₆₀, and paraffin oil were purchased from Sigma-Aldrich. Mercaptobenzoic acid (MBA), 3-dihydro-1H-isoindole, HPLC grade methanol, and toluene were purchased from Sigma or Rankem. Au and Ag nanoparticles (Au NPs and Ag NPs) were synthesized in the laboratory following the reported methodology.^{18,19} Pure coconut oil was prepared by a standard

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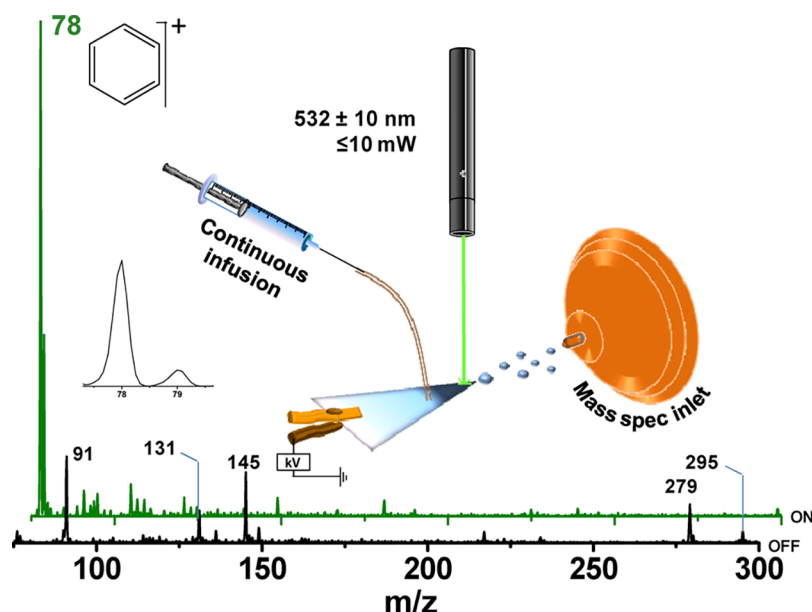


Figure 1. Mass spectrum of benzene in presence (green trace) and absence of laser (black trace). Inset shows schematic of the experimental setup of laser assisted paper spray ionization mass spectrometry (LAPSI MS). A green diode laser was pointed at the tip of the paper with a continuous supply of analyte through a fused silica capillary. The figure is not to scale. Peaks in the laser-off condition are due to the background, indicating impurities on the paper.

protocol by milling. Adulterated coconut oil samples were purchased from the local market.

LAPSI MS. In LAPSI MS, we have introduced a green laser pointer (532 ± 10 nm, ≤ 10 mW), (UKTECHLAB, U.K.) along with standard paper spray mass spectrometry. The inset of the Figure 1 schematically demonstrates the experimental setup. A Thermo Scientific LTQ XL mass spectrometer was used for all of the mass spectrometric measurements. A Whatman 42 filter paper was cut into a triangular shape (Figure S1) and was connected to a high voltage power supply through a copper clip in such a way that one of the vertices was pointed toward the inlet of the mass spectrometer. The average area of the paper was 3.2 cm^2 for all of the experiments. The distance between the tip of the paper and the mass spectrometer inlet was set to be 10 mm in all the cases. The laser was placed vertically at a distance of 10 cm from the paper. The laser spot was the tip of the paper, and the visible spot diameter was approximately 3 mm. Although the laser runs on a battery, it was connected to a switch mode power supply (SMPS) to give constant input power, enabling constant laser intensity throughout the experiments. The spray voltage was varied from 1 to 5 kV depending on the analyte.

The capillary and tube lens voltages were set to ± 45 and ± 100 V for positive and negative modes, respectively. The capillary temperature was 250°C , and the sheath gas pressure was set to zero. The solvent or the analyte solution was continuously supplied to the paper through a fused silica capillary ($300 \mu\text{m}$ outer diameter, $100 \mu\text{m}$ inner diameter), connected to a $500 \mu\text{L}$ Hamilton gas-tight syringe, using a syringe pump. The solution infusion rate was optimized by trial and error to be $8 \mu\text{L}/\text{min}$ for all our experiments. Methanol, toluene, and a mixture of these two solvents were used as solvents for experiments such as in situ dehydrogenation, ionization of C_{60} , and ionization of polycyclic aromatic hydrocarbons.

Synthesis of Au NPs. Citrate protected Au NPs were synthesized by the reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with trisodium

citrate using the Turkevich method.¹⁸ About 10 mL of an aqueous solution of $5 \text{ mM HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was taken and diluted with 180 mL of distilled water followed by heating until it started boiling. An aqueous solution of trisodium citrate (10 mL, 0.5%) was added to it and then heated again until the solution become wine red in color. The solution was cooled and used directly as the catalyst for in situ monitoring of laser-induced transformations.

Synthesis of Ag NPs. The Turkevich method was used for the synthesis of citrate protected Ag NPs.¹⁹ About 40 mg of trisodium citrate was added to a 1 mM aqueous solution of silver nitrate at 100°C , and the solution was heated until a pale yellow color was observed. The final solution was cooled and used in LAPSI MS.

Monitoring in Situ Chemical Reactions. Citrate protected Au NPs and Ag NPs were drop cast over the filter paper and kept for drying under laboratory conditions. It was cut into a triangular shape for LAPSI MS measurements. The spray voltage was set to 3 kV during the experiment. In the case of the decarboxylation reaction,²⁰ an ethanolic solution of MBA ($50 \mu\text{M}$) was used as the reactant. For the dehydrogenation reaction,²¹ a 50 pM solution of 2,3-dihydro-1*H*-isoindole in methanol was pushed directly to the paper source, and the mass spectrum was collected in presence and absence of the laser.

Detection of Adulteration in Coconut Oil. A mixture of methanol and toluene (1:1 (V/V) ratio) was used to make the solution of both paraffin oil and coconut oil. Pure coconut oil was used as the standard sample. Standard mixtures were made by mixing paraffin oil (1, 5, 10, 20, and 30%) in a solution of coconut oil. Experiments were conducted in two different ways. In the first case, we spotted the oil on the paper source and then eluted it with a solvent mixture to collect the mass spectrum. In the second case, the solution of oil was fed to the paper source continuously. The data were compared with those of the adulterated sample of the oil obtained from the market.

DFT Calculations. The structures of all the analytes were optimized at the level of theory consisting the hybrid B3LYP

DFT functional^{22,23} and cc-pvtz basis set²⁴ as implemented in the Gaussian 09 software package.²⁵ The vibrational frequencies were also calculated to confirm that the optimized structures are on local minima along the potential energy surface. The IP of analytes is calculated with and without application of the electric field by subtracting the energy of neutral analytes from their ionic state. The IPs are calculated by varying the applied electric field from 0 to 500 MV/cm on all three axes (x , y , z) and are plotted. The electric field is modeled by applying an electric dipole field by defining 0.0002 au for 1 MV/cm in all three directions.

RESULTS AND DISCUSSION

Characterization of LAPSI MS. In standard paper spray, molecules like benzene cannot be ionized. However, LAPSI MS

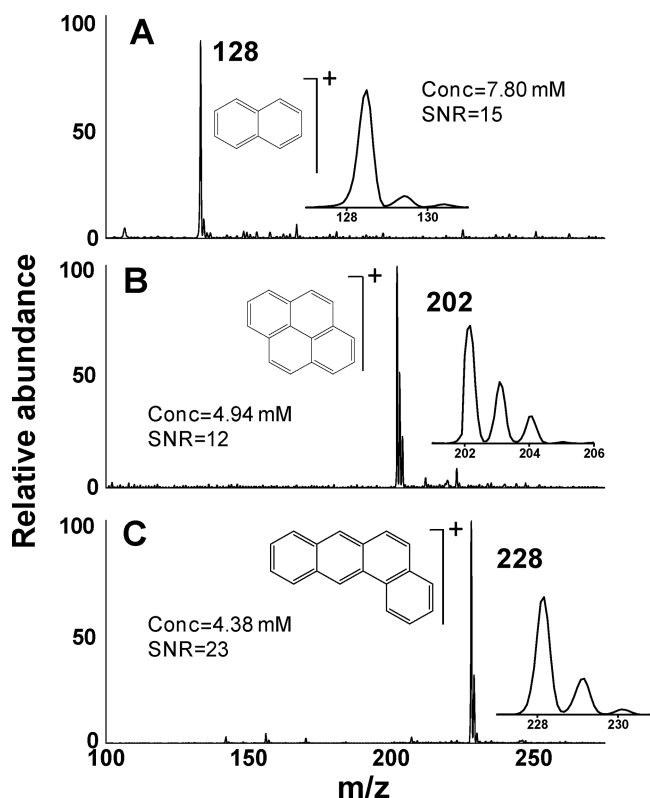


Figure 2. LAPSI MS spectra of PAHs: (A) naphthalene, (B) pyrene, and (C) benzantracene in positive ion mode. Isotope distributions of the species are shown.

gives a clean spectrum for benzene with an isotopic distribution (Figure 1). The peak corresponding to benzene disappeared completely in the absence of the laser. This shows that LAPSI MS can be a potent method to ionize hydrocarbons that cannot be ionized easily in standard paper spray conditions.

The same methodology can be applied to ionize other aromatic hydrocarbons. Figure 2A–C shows the mass spectra collected for naphthalene, pyrene, and benzantracene, respectively, in positive mode, where the peaks at m/z 128, 202, and 228 represent the molecular cations of the respective analyte. The inset shows the isotopic distributions in all cases. It clearly shows that LAPSI MS has the capability to ionize certain types of molecules in their molecular ion form, and polycyclic aromatic hydrocarbons are one such category.

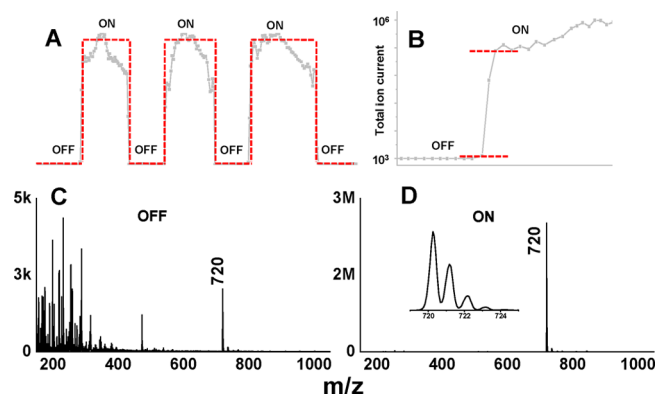


Figure 3. (A,B) Selected ion chromatogram for m/z 720 under laser-on/off conditions. (C,D) Mass spectrum of C_{60} in negative mode in the absence and presence of laser, respectively. Inset in D shows the isotopic distribution of C_{60} . Compare the intensities of C and D (5k vs 3M) or (5×10^3 vs 3×10^6).

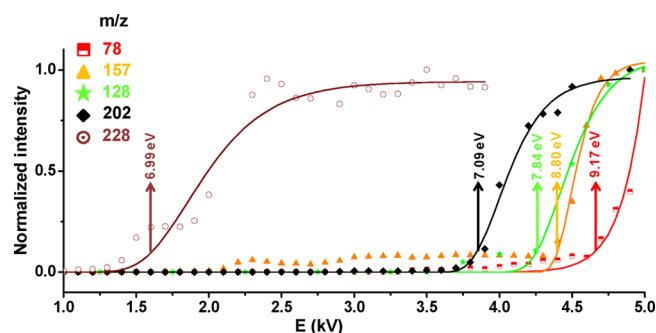


Figure 4. Voltage dependence in the ion intensity of benzene (m/z 78), bromobenzene (m/z 157), naphthalene (m/z 128), pyrene (m/z 202), and benzantracene (m/z 228). Arrows indicate the IPs of the analytes measured.

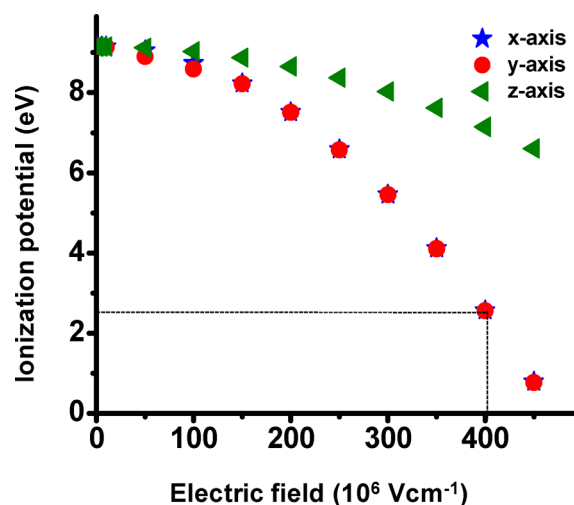


Figure 5. Calculated IPs of benzene in the presence of high electric fields along x , y , and z directions. Ionization threshold at 2.3 eV is marked.

The effect of laser-induced enhancement in ionization is dramatic in the case of C_{60} . Figure 3 illustrates 10^3 fold enhancement in the molecular ion intensity of C_{60} in the presence of laser. The laser was switched on and off in a periodic fashion approximately at the same time interval. The

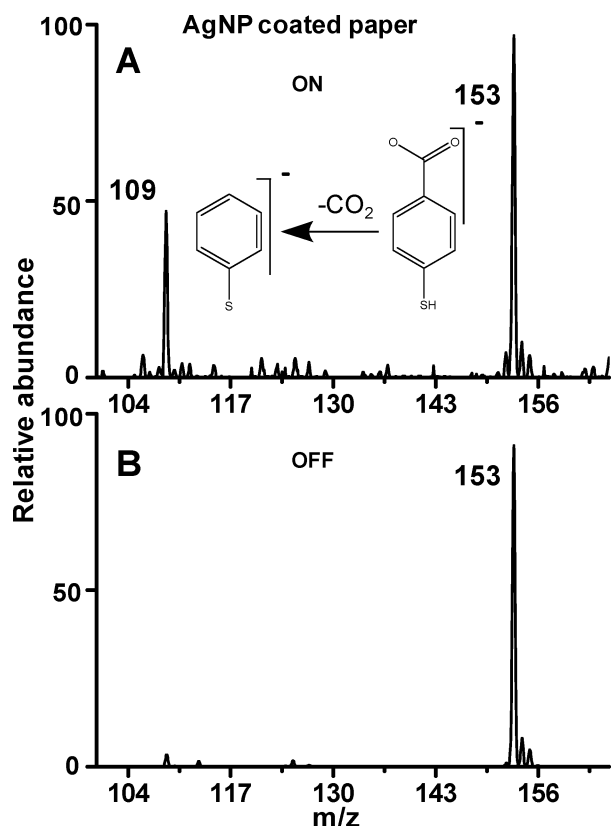


Figure 6. In situ monitoring of decarboxylation reaction on Ag-NP-coated paper in (A) presence and (B) absence of laser.

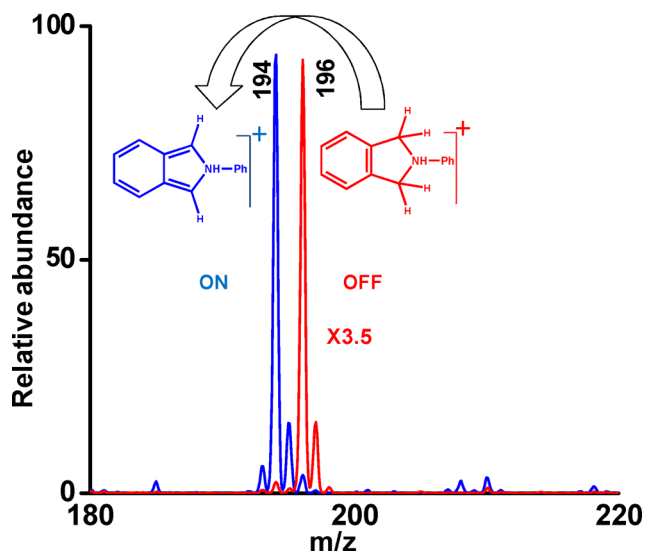


Figure 7. Mass spectrum collected for the dehydrogenation reaction of 3-dihydro-1H-isoindole.

chronogram in Figure 3A is a selected ion chronogram for the peak at m/z 720 (molecular anion of C_{60}). It clearly reflects the enhancement of the C_{60} signal intensity in the presence of laser. Figure 3C,D allows us to compare the mass spectrum taken for C_{60} (1 mg/mL or 1.39 mM) in laser-off and laser-on conditions. The intensity of the molecular ion is so high that we cannot see any background in this case. These results indicate that the LAPSI MS method works well both in positive and negative ion modes. Concerning the limit of detection of

this ionization, we note that the method can detect analytes at a concentration of 1.04 nM taking C_{60} as an example. Quantification was possible as demonstrated from real samples, and this will be discussed later. We note that quantitative analysis of C_{60} was possible in the laser-off condition also (Figure S7).

LAPSI MS is an ambient ionization technique involving a low power laser along with a high voltage of the standard paper spray method. The mechanism of ionization is different from the usual laser desorption ionization techniques where a high energy laser is used directly to produce ions such as in matrix assisted laser desorption ionization (MALDI),²⁶ laser desorption/ionization (LDI),²⁷ or techniques involving a laser and electrospray, such as electrospray assisted laser desorption ionization (ELDI)²⁸ and laser ablation electrospray ionization (LAESI).²⁹ It has also been shown that a UV pulsed laser produces soft ionization during DESI imaging due to the solvent cage effect.³⁰ In order to understand the mechanism of the observed ionization event, ion yield was measured from the selected ion chronogram of various analytes with increasing electric field. Plot of normalized intensity vs applied potential shown in Figure 4 proves the direct correlation between ionization potential (IP) and applied voltage.

The field assisted photo ionization can be explained with the example of benzene. With a 532 nm laser, the available photon energy is 2.33 eV. Therefore, without the assistance of an electric field, the photon energy is inadequate to cause ionization, as the IP of benzene is 9.17 eV. For an applied potential of 4.8 kV, which can be termed as threshold potential, the benzene molecules feel an electric field of more than 10^7 V cm^{-1} at the sharp tip of the triangular paper.³¹ This is due to the fact that the molecules are trapped in between the fibers of the paper. Figure S1 shows a scanning electron microscopy image (SEM) of the triangularly cut paper. Where we can see that the diameter of the fibers at the tip of the paper is in the range of 10 to 20 μm , which produces a sufficient electric field for ionization. This electric field causes a distortion of the ground state to a large extent, which brings down the ionization potential to 2.33 eV. Depending on the π system of the molecule, the threshold ionization voltage varies. From Figure 4, it shows that the threshold ionization voltage decreases with increasing π electron density in the molecule. In the case of benzene, the threshold voltage is around 4.8 kV, and at the same time, benzantracene needs only around 2.5 kV to start ionization.

Density functional theory (DFT) was useful in understanding the change in IP of the analytes. Field dependent IP was calculated using different methods.^{32,33} Herein, the field dependent IP has been calculated at B3LYP/cc-pVDZ level of theory. Figure S2A–E shows the energy optimized structures for benzene, bromobenzene, naphthalene, pyrene, and benzantracene and their orientations with respect to the applied electric fields. Figures 5 and S3A–D show the IPs for all the analytes in the presence of electric fields ranging from 0 to 500 MV/cm along all the three axes. Due to the high IP of benzene (9.17 eV, calculated at zero field), it required a larger electric field for ionization. In general, for all the molecules, the influence of electric field on the IP along the z axis is less in comparison to other axes. This may be because the molecules are planar, and the field is considered normal to that plane.

Although IP at low electric fields (up to 100 MV/cm) differs slightly along the x and y axes for benzene, the calculated IPs are invariant at higher electric fields as shown in Figure 5, and it

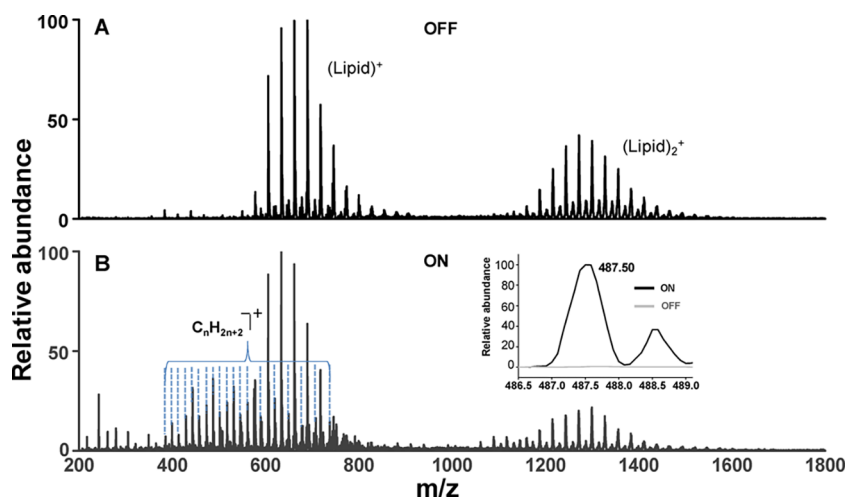


Figure 8. Mass spectrum of coconut oil, sold in local market recorded in (A) absence and (B) presence of the laser. A specific region is expanded in the inset to show the difference.

is attributed to the high molecular symmetry (D_{6h}) of benzene. When the field reaches 408 MV/cm, the IP is reduced to 2.3 eV along both the axes. Hence, benzene exhibits ionization when the laser is applied at this electric field. In support to the speculated mechanism, other analytes studied also follow a similar behavior. Figure S3 shows a clear decrease in the threshold ionization voltage with increasing electron density in the system.

Control experiments were performed to check the importance of the laser in LAPSI MS. Figure S4 shows that there is no ionization in the absence of laser even up to 5 kV of spray voltage for benzantracene and bromobenzene. However, ionization occurs in the presence of laser. Figure S4 also shows comparison of LAPSI with ESI and standard PSI using benzantracene as the analyte (all the parameters were the same in all cases). ESI as well as standard PSI do not show a peak at m/z 228 due to benzantracene, while LAPSI shows an intense signal. Hence, both ESI and PSI are inadequate to detect the molecule. This result clearly indicates that the ionization mechanism of LAPSI MS is distinctly different from that of ESI and also from that of field enhanced ionization of PSI.³¹

We speculate that the enhanced ionization of C_{60} in the negative ion mode follows a one electron capture mechanism. The ionization involves solvent ionization first followed by capture of the released electron by the un-ionized C_{60} molecule. Figure S5 shows that the enhancement in signal intensity in the case of C_{60} in the negative ion mode equals approximately the intensity enhancement for toluene in the positive ion mode, in the presence of laser. These results support the speculated mechanism of electron capture by C_{60} . For further confirmation of the mechanism, we have taken C_{60} in two different solvents, dichloromethane (DCM) and chloroform, which are unresponsive to LAPSI MS in the studied potential range. Figure S6B,C presents the results where we can see from the selected ion chronogram that the intensity of m/z 720 remains constant during the laser-on and -off conditions in both DCM and chloroform but was increased in the case of toluene (Figure S6A). This confirms the mechanism. While enhancement was detected for C_{60}^- , a similar effect has not seen for analytes forming positive ions. This may require the use of a proper electron capturing agent.

Monitoring an in Situ Photochemical Reactions by

LAPSI MS. LAPSI MS provides extra advantages, as it involves irradiation of a laser on the paper, which allows one to monitor photochemical reactions. Figure 6 presents decarboxylation of *p*-MBA over Ag nanoparticle-coated paper. During the laser-off condition, the detected mass peak at m/z 153 corresponds to *p*-MBA [$M - H$] in the negative ion mode over Ag NP-coated paper (Figure 6B). But when the laser was turned on, a peak at m/z 109, which corresponds to the decarboxylated product of *p*-MBA appeared (Figure 6A). A similar result was seen in the case of Au NP-coated paper (Figure S8).

We have also performed a dehydrogenation reaction on 2,3-dihydro-1*H*-isoindole in the presence of the laser. Figure 7 shows the mass spectrum of the reaction during laser-on and -off conditions. The peak at m/z 196 is the molecular ion of 2,3-dihydro-1*H*-isoindole in the positive ion mode during the laser-off condition. When the laser was turned on, the molecule loses two hydrogens to get aromatized, and the product peak at m/z 194 was formed.

Detection of Hydrocarbons as Adulterants in Coconut Oil by LAPSI MS.

In order to use this methodology in an analytical context, we chose to study the adulteration of vegetable oils by mineral oils, which is a common problem in many countries. As shown in Figure 8, LAPSI MS was able to detect the presence of paraffin oil in commonly sold coconut oil, purchased from the market. It is important to note that paraffin oil is undetectable in conventional paper spray or by electrospray ionization. By preparing a standard sample and correlating the intensity of the selected ion at m/z 487.50 (which corresponds to the average mass of species, $C_{33}H_{59}O_2^+$, $C_{34}H_{63}O^+$, and $C_{35}H_{67}^+$ (Figure S9), which are present in the mass spectrum of paraffin oil³⁴), we found that the extent of contamination is about 10%. Figure S10 provides the chronogram and the mass spectrum of pure paraffin oil by LAPSI MS. The envelope of mass peaks in the spectrum correspond to the hydrocarbons present in the paraffin oil. Figure S11 represents the mass spectrum taken for pure coconut oil, where the first bunch of mass peaks corresponds to the lipids present in the coconut oil. The next bunch of lipids are the dimers of the same. In this range, upon application of laser, no additional peak was observed.

CONCLUSIONS

In conclusion, we have introduced a new form of paper spray mass spectrometry called laser assisted paper spray ionization mass spectrometry (LAPSI MS), useful for the detection of saturated and unsaturated hydrocarbons, by including a simple 532 ± 10 nm, ≤ 10 mW green pointer laser to it. This method extends the scope of ambient ionization. We show that the photoionization is field assisted from various control experiments. Solvent-induced ionization enhancement of C_{60} has also been demonstrated. We show the capability of the system to monitor some of the photoinduced transformations in situ. We hope that this analytical methodology will be useful for the easy detection of analytes in diverse situations. As ionization is photoassisted, use of other light sources is possible by varying the threshold potential used for ionization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b05213.

SEM of the paper, details of DFT calculations, control experiments, mass spectra of pure paraffin, coconut oil, and a standard mixture of the two (PDF)

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Notes

The authors declare no competing financial interest.

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