



**INTELLECTUAL
PROPERTY INDIA**

PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS



सत्यमेव जयते

भारत सरकार
GOVERNMENT OF INDIA

पेटेंट कार्यालय
THE PATENT OFFICE

पेटेंट प्रमाणपत्र
PATENT CERTIFICATE
(Rule 74 Of The Patents Rules)

क्रमांक : 044123586
SL No :



पेटेंट सं. / Patent No. : 348929
आवेदन सं. / Application No. : 6137/CHE/2013
फाइल करने की तारीख / Date of Filing : 30/12/2013
पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER नामक आविष्कार के लिए, पेटेंट अधिनियम, 1970 के उपबंधों के अनुसार आज तारीख 30th day of December 2013 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER as disclosed in the above mentioned application for the term of 20 years from the 30th day of December 2013 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 09/10/2020
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

Okrajt

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 30th day of December 2015 को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 30th day of December 2015 and on the same day in every year thereafter.

6137/CHE/2013

FORM 2
THE PATENTS ACT, 1970
(39 OF 1970)
&
The Patents Rules, 2003
COMPLETE SPECIFICATION
(Refer section 10 and rule 13)

23 JUL 2014

TITLE OF THE INVENTION:

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

2. APPLICANTS

APPLICANT 1:

(A) NAME: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS**

(B) NATIONALITY: Indian

(C) ADDRESS: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS**

IIT P.O. Chennai - 600 036

APPLICANT 2:

(A) NAME: **PURDUE RESEARCH FOUNDATION**

(B) NATIONALITY: USA

(C) ADDRESS: **Purdue Research Foundation, 1281 Win Henschel Blvd., West Lafayette, IN 47906**

ORIGINAL

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

FIELD OF THE INVENTION

The invention relates generally to ionization for mass spectrometers, and, more particularly, to impregnated ion source used to generate ions from organic molecules under low electric potentials.

BACKGROUND OF THE INVENTION

Recent progress in mass spectrometry has depended heavily on advances in methods of ion formation. Creation of stable molecular ions of complex molecules with minimum internal energy has been a primary goal of such experiments. The most widely used methods to achieve this are electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI). The newer ambient ionization methods [M. E. Monge, G. A. Harris, P. Dwivedi, F. M. Fernandez, *Chem.Rev.* 2013, 113, 2269-2308] such as desorption electrospray ionization (DESI) [Z. Takats, J. M. Wiseman, B. Gologan, R. G. Cooks, *Science* 2004, 306, 471-473] allow samples to be examined in their native state with minimal or no sample pre-treatment. These advantages and the resulting speed of analysis have led to the introduction of some fifty different variants of ambient ionization. Direct analysis in real time (DART), [R. B. Cody, J. A. Laramee, H. D. Durst, *Anal. Chem.* 2005, 77, 2297-2302] extractive electrospray ionization (EESI) [a) X. Zhang, N. Wang, Y. Zhou, Y. Liu, J. Zhang, H. Chen, *Anal. Methods* 2013, 5, 311-315; b) G. A. Harris, A. S. Galhena, F. M. Fernandez, *Anal. Chem.* 2011, 83, 4508-4538], desorption atmospheric pressure chemical ionization (DAPCI) [Z. Takats, I. Cotte-Rodriguez, N. Talaty, H. Chen, R. G. Cooks, *Chem. Commun.* 2005, 1950-1952], desorption atmospheric pressure photoionization (DAPPI) [M. Haapala, J. Pol, V. Saarela, V. Arvola, T. Kotiaho, R. A. Ketola, S. Franssila, T. J. Kauppila, R. Kostainen, *Anal. Chem.* 2007, 79, 7867-7872], laser ablation electrospray ionization (LAESI) [G. A. Harris, A. S. Galhena, F. M. Fernandez, *Anal. Chem.* 2011, 83, 4508-4538] and paper spray ionization [J. Liu, H. Wang, N. E. Manicke, J.-M. Lin, R. G. Cooks, Z. Ouyang, *Anal. Chem.* 2010, 82, 2463-2471] are some of the new methods introduced over the past decade. Here, we show that ionization can be achieved from a substrate coated with carbon nanotubes (CNTs) at a potential difference of just a few volts. The high electric fields produced at the small CNT protrusions are suggested to be the reason for low voltage ionization which appears to occur by field emission of charged microdroplets [a) X. Xu, W. Lu, R. B.

Cole, *Anal. Chem.* **1996**, *68*, 4244-4253 b) G. Wang, R. B. Cole, *Anal. Chim. Acta* **2000**, *406*, 53-65]. Various analytes applied to the tip of the coated paper are detected using mass spectrometry (MS).

In this method of ion formation, neutral molecules typically appear as either their protonated or deprotonated forms while salts yield both positive and negative ions. The fact that a high voltage (HV) is not needed sets this method apart from most other spray-based ambient ionization methods.

SUMMARY OF THE INVENTION

The present invention relates to an ionization source for use in MS, wherein the said ionization source is a modified paper surface.

Wherein the paper modification is characterized by impregnations or coatings made with nanoscale sized features selected from CNT.

Wherein the invention is characterized to generate and analyse ions from a wide variety of compounds / analytes including organic compounds and common pesticides, ingredients of medicinal tablets, amino acids, etc.

Wherein ambient ionization is achieved by spraying from a CNT-impregnated paper surface under the influence of small voltages especially at potentials as low as (\geq) ± 3 V.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 A) shows a schematic diagram of ionization from CNT paper, B) photograph of ionization source showing paper triangle and battery along with a grounding electrical connection, C) mass spectra of triphenylphosphine (M) at 3 kV, 3 V and 1 V from wet CNT paper, D) field emission-scanning electron microscopy (FE-SEM) image of CNT-coated paper, E) isotope distribution of the protonated molecule at 3 V and F) product ion MS² of m/z 263.

Fig. 2 shows full range mass spectrum of triphenylphosphine at 3 V.

Fig 3 shows ESI mass spectrum (MeOH:H₂O, 1:1) of triphenylphosphine at 3 kV. The spectrum shows an enhanced oxidation peak at m/z 279 and its C₆H₆ fragment at m/z 221, in comparison to the CNT-coated paper (Figure 1C). MS/MS spectrum is shown in the inset.

Fig. 4 shows A) mass spectrum of TPP below 500 V using normal paper as seen on the spectrometer (no signal is seen), B) spectrum of TPP at 3 V using CNT-coated paper (same as that in Figure 1C, given for comparison), C) spectrum at 500 V from a normal paper, D) spectrum using rectangular CNT-coated paper and the inset shows the schematic of the paper (with mass spectrometer facing it), E) variation of

intensity of the m/z 263 peak with voltage for CNT-coated paper and F) the same for normal paper.

Fig. 5 shows intensity enhancement upon the addition of dil. HCl for various analytes (M) at 3 V, A) triphenylphosphine, B) tributylphosphine, C) diphenylamine and D) triethylamine. The upper and lower traces in each plot are on the same scale and show spectra before and after HCl addition, respectively.

Fig. 6 illustrates the analysis of preformed ions (positive and negative ion modes) at 3 V; A) tetramethylammonium chloride and B) tetramethylammonium bromide.

Fig. 7 illustrates the analysis of preformed ions (positive and negative ion modes) at 3 V; A) tetramethylammonium nitrate and B) tetrabutylammonium iodide.

Fig. 8 shows detection of pesticides examined individually from the surface of an orange. A) Carbofuran, B) methyl parathion and C) parathion.

Fig. 9 illustrates the analysis of a pesticide mixture at 3 V from the surface of an orange. Isotopic distribution of the peaks is not clearly visible due to low intensity.

Fig. 10 illustrates the analysis of tablets from CNT-coated paper at 3 V with their mass spectral and MS² data. A) Crocine (paracetamol), B) xyzal (levocetirizine dihydrochloride) and C) combiflam (paracetamol).

Fig. 11 illustrates the detection of various amino acids (90 ng) loaded on CNT-coated paper and spectra recorded at 3 V: A) phenylalanine, B) methionine, C) glutamic acid, D) glutamine, E) isoleucine, F) valine, G) proline and H) serine.

Fig. 12 shows Raman measurement of CNT-coated paper before and after ionization. A) Neutral molecules (30 ppm TPP in MeOH/H₂O) and preformed ions (tetramethylammonium bromide) in B) positive and C) negative ion modes.

Referring to the drawings, the embodiments of the present invention are further described. The figures are not necessarily drawn to scale, and in some instances the drawings have been exaggerated or simplified for illustrative purposes only. One of ordinary skill in the art may appreciate the many possible applications and variations of the present invention based on the following examples of possible embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an ionization source for use in mass spectrometry, wherein the said ionization source is a modified paper surface.

Wherein the paper modification is characterized by impregnations or coatings made with nanoscale sized features selected from CNT.

Wherein the invention is characterized to generate and analyse ions from a wide variety of compounds / analytes including organic compounds and common pesticides, ingredients of medicinal tablets, amino acids, etc.

Wherein ambient ionization is achieved by spraying from a CNT impregnated paper surface under the influence of small voltages especially at potentials as low as (\geq) ± 3 V.

Ambient ionization is achieved by spraying from a CNT impregnated paper surface under the influence of small voltages (≥ 3 V). Organic molecules give simple high quality mass spectra without fragmentation in the positive or negative ion modes. Conventional field ionization is ruled out and field emission of microdroplets is indicated. Microscopic examination of the CNT paper confirms that the nanoscale features at the modified paper surface are responsible for high electric fields. Raman spectra imply substantial current flow in the nanotubes. Analytical performance is shown with volatile and non-volatile compounds and a variety of matrices.

Experiments were done with triangles of CNT-coated paper, wet with MeOH/water and connected to a 3 V battery (Figure 1A, B); more details are presented in the experimental section. Mass spectra recorded for triphenylphosphine (TPP) using the CNT paper and 3 V battery source (Figure 1C) exhibited a peak at m/z 263 due protonated TPP, $[M+H]^+$. Spectra could be collected for 2-3 sec using 2 μ L of solvent. When the voltage on the paper was reduced to 1 V, the spectrum disappeared completely. The full range mass spectrum of TPP on CNT-coated paper (Figure 2) is similar to the ESI mass spectrum recorded at 3 kV (Figure 3). Although the intensity of the molecular ion at 3 V is as much as 10^4 times less than that seen in ESI, the conditions are less harsh, in particular the oxidation product at m/z 279 as well as that of a trace homologous impurity (product at m/z 293) are absent, as are their fragmentation products at m/z 203 and m/z 219. Moreover, the mass spectrum shows a well-defined isotopic pattern (Figure 1E) of the molecular ion and confirmation of its structure comes from tandem mass spectrometric data (Figure 1F) which show the expected benzene loss and associated further loss of H_2 upon collision induced dissociation.

An increase in the applied potential increases the ion intensity, saturating at 4 kV, at which point the signal was almost of the same magnitude as the ESI signal. However, no additional features were observed. The two spectra (at 3 kV and 3 V, both from CNT coated paper) shown in Figure 1C are identical in terms of the ions observed. A minimum applied voltage of 3 V is essential for detectable ion signals. Control experiments confirmed the fact that CNTs were essential in the ionization process at 3 V. Filter paper (without the CNT-coating) but cut similarly and using the same solvent does not produce

detectable ions with a range of analytes, even up to 500 V (Figure 4A). Closer examination of the edge of the paper shows protruding nanotubes (Figure 1D). From these results and experiments described below, we suggest that field emission of microscale solution droplets containing analyte occurs at these nanoscale protrusions and this is responsible for the observed ionization event.

Additional experiments were conducted to explore the mechanism of ionization. Clearly the absence of fragment ions in the mass spectrum may be attributed to the occurrence of soft ionization events. The occurrence of ionization at 3 V strongly implies a process associated with a very high electric field. The field must be due to the small conductive CNT structures (Figure 1D) protruding from the surface of the filter paper and acting as an electrode [B. Gruener, M. Jag, A. Stibor, G. Visanescu, M. Haeffner, D. Kern, A. Guenther, J. Fortagh, *Phys. Rev. A: At., Mol., Opt. Phys.* 2009, 80, 063422/063421-063422/063427]. The voltage (from the battery) applied at the CNT electrode induces an electric field between the paper tip and the mass spectrometer inlet. The field intensity is high at the paper tip, where ionization occurs.

To differentiate the contributions of the protruding CNT structures and macroscopic paper tip to ionization, another experiment was done where a rectangular CNT-coated paper was held in front of the mass spectrometer inlet (with one of the long sides facing the MS inlet) and ionization of TPP was attempted. All other parameters except the shape of the paper were held constant. The mass spectra showed (Figure 4D) ionization of TPP at 3 V from this paper rectangle. This proves that there is no involvement in this case of the pointed paper tip but the protruding CNTs are responsible for ionization. Also the complete absence of molecular ion peaks while using a similarly cut filter paper (without CNT coating) reveals the role of nanoscale CNTs in providing a field strength high enough to cause field emission. Figures 4E and 4F show the change in intensity of the molecular ion peaks with voltage for CNT-coated and normal paper triangles, respectively. The ion signals for both these papers saturate at high voltages, but with CNTs, the onset of ion ejection is much earlier. Thus from these experiments it is reasonable to conclude that at lower voltages CNTs play a role in ionization and with the increase of voltage a Taylor cone forms at the paper tip and the macroscopic electric field is responsible for ionization.

In conventional field ionization [a) J. Luo, L. P. Mark, A. E. Giannakopoulos, A. W. Colburn, J. V. MacPherson, T. Drewello, P. J. Derrick, A. S. Teh, K. B. K. Teo, W. I. Milne, *Chem. Phys. Lett.* 2011, 505, 126-129; b) A. Goodsell, T. Ristroph, J. A. Golovchenko, L. V. Hau, *Arch., Phys.* 2010, 1-12], vapor phase molecules placed in a strong electric field lose an electron to form positively charged radical

cations. Many of the analytes used are simple volatile organic molecules which if ionized by this mechanism would be expected to give M^+ radical cations, e.g. m/z 262 in the case of TPP, not the observed m/z 263. To test whether field ionization of vapour phase triethylamine might contribute, triethylamine (vapor pressure = 57 torr at 20°C) was dissolved in acetone (vapor pressure = 184.5 torr at 20°C) and introduced into the field (the gap between CNTs and MS inlet) as the vapor and ionization was attempted at low voltages. The results showed that analyte vapors do not give detectable ionization. We conclude that field emission occurs from a solvated analyte or droplet, as in all cases only $[M+H]^+$ and not the radical cation M^+ was detected.

To further test the proposed field emission of charged droplet mechanism, the experiment with TPP and three other analytes was repeated in the presence and absence of added protic acid [N. B. Cech, C. G. Enke, *Mass Spectrom Rev* 2001, 20, 362-387]. Addition of acid will generate the salt and should inhibit simple field ionization (to give M^+) but it should increase the field emission/ionization from droplets (to give $M+H^+$). For this reason, particular analytes were selected which contain basic functional groups (phosphines and amines) and they were analysed before and after addition of dilute acid (HCl). Figure 5 shows enhancement in relative intensity of the protonated molecules after the addition of dilute acid to analytes which contain basic functional groups. This enhancement supports ionization of a solvated species.

Various preformed ions (derived from salts like tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium nitrate and tetrabutylammonium iodide) were studied under the same conditions. In accordance with the proposed mechanism, both positive and negative ions were observed in the CNT-derived mass spectra (Figure 6 and 7). No fragmentation was observed and the extreme softness of the process compared even to other soft ionization methods is indicated by the presence of hydrated halide anions. These studies show that preformed ions can also be ejected from the surface in droplets and conventional field ionization is not responsible for ion formation.

To further characterize the CNT-ionization technique, it was employed for qualitative analysis of various analytes including pesticides, antibiotics and amino acids. All gave characteristic mass spectra; hence this low voltage ionization methodology is shown to be useful for diverse analytical needs. Direct analysis of various contaminants on fruits is possible with this methodology. Three common insecticides (carbofuran, methyl parathion and parathion) used for the protection of fruits were applied on the surface of an orange at 50 ppm concentration. Then CNT-coated paper was rubbed on the surface and held in

front of the MS inlet for analysis. Figure 8 shows molecular ion peaks of different pesticides using the battery spray MS method. In reality, the amount of sample extracted from the fruit surfaces during rubbing may be several orders of magnitude lower than the applied quantity and so the limit of detection is much lower than the applied sample concentration. Figure 9 shows the molecular ion peaks of each of these pesticides from their mixture.

The same methodology was used to analyse medicines. CNT coated paper was rubbed on the surfaces of three commercially available medicinal tablets, viz. crocin, combiflam and xyzal (trade names) and held in front of a MS inlet with the 3 V battery set-up. Figure 10 show that both crocin and combiflam contain paracetamol (acetaminophen) as the major ingredient. Direct analysis of these tablets using CNT-coated paper gave a peak corresponding to protonated paracetamol. The other tablet, xyzal is a non-sedative antihistamine and contains levocetirizine dihydrochloride as the active ingredient. Analysis of this tablet (Figure 10B) under the same conditions gave protonated levocetirizine. The identity of the analytes was confirmed by MS² studies (data shown in the insets).

Direct analysis of amino acids is also possible by spraying from CNT-coated paper. Several amino acids (30 ppm) were dropped onto the tip of the CNT-coated paper with a micropipette (injected volume 3 μ L, corresponding to a total loading of 10 ng). Figure 11 shows intense protonated molecular peaks of the amino acids. The zwitterionic nature of amino acids may lead to easy extraction of ions from the nanotube tips in the electric field.

In order to probe the effect of the ionization event on the paper electrode itself, Raman spectra of CNT-coated paper were recorded before and after a series of experiments (ionization of TPP at 3 V over a period of 20 minutes) (Figure 12A) [a] S. Costa, E. Borowiak-Palen, M. Kruszynska, A. Bachmatiuk, R. J. Kalenczuk, *Mater. Sci.-Pol.* 2008, 26, 433-441; b) A. Naeemi, J. D. Meindl, *Annu. Rev. Mater. Res.* 2009, 39, 255-275]. The data show a large red shift [a] S. Lee, J.-W. Peng, *J. Phys. Chem. Solids* 2011, 72, 1101- 1103; b) G. M. Bhalerao, M. K. Singh, A. K. Sinha, H. Ghosh, *Phys. Rev. B: Condens. Matter Mater. Phys.* 2012, 86, 125419/125411-125419/125416] in the D and G bands which implies the acquisition of electrons in the CNT during positive mode ionization [B. Scheibe, E. Borowiak-Palen, R. J. Kalenczuk, *Mater. Charact.* 2010, 61, 185-191]. It appears that as ionization occurs, charge builds up as would be expected for a field-assisted ionization [a] J. Luo, L. P. Mark, A. E. Giannakopoulos, A. W. Colburn, J. V. MacPherson, T. Drewello, P. J. Derrick, A. S. Teh, K. B. K. Teo, W. I. Milne, *Chem. Phys. Lett.* 2011, 505, 126-129; b) A. Goodsell, T. Ristroph, J. A. Golovchenko, L. V. Hau, *Arch., Phys.* 2010, 1-12]. However, there appears to be electron transfer from the developing microdroplet to the CNT; effectively a polarization of the electrons in the long thin CNT fiber (see Figure 1D) driven by the high

field and mobility of electrons in the CNTs and its large electron affinity [M. Shamsipur, M. Asgari, M. F. Mousavi, R. Davarkhah, *Electroanalysis* 2012, 24, 357-367]. As the positively charged droplet breaks away, the residual charge appears to lead to reduction of CNTs as reflected in the Raman spectrum as red-shifted D and G bands. This speculation on electron transfer from the charged micro droplet of solvent to CNT was supported by a blank experiment, where only solvent and potential were applied to CNT-coated paper for the same period of time and Raman measurement was performed. The spectrum showed red shifts in D and G bands.

The Raman spectra of the nanotube sample were also recorded before and after ionization of the salt tetramethylammonium bromide in both the positive and negative ion modes. Figure 12B shows a red shift of D and G bands for CNT-coated paper in case of the positive ion mode measurement. This may be due as before to the high electric field needed to cause solvated ion ejection as micro droplets. There was no such reduction for the negative ion mode measurement as Raman measurements show unshifted D and G bands, (Figure 12C) presumably because the CNTs are already electron-rich in this condition and the field replenishes the charge lost.

The results presented here suggest a versatile strategy for the direct analysis of diverse chemical species. The methodology can be modified to suit various analytical requirements. Replacement of the high voltage power supply with a 3V battery simplifies mass spectrometry through ion formation from a nanoscale antenna. The CNT ionization method has been applied to a variety of samples from different sources including fruit surfaces, medical tablets, and a range of organic molecules, including amino acids, antibiotics and pesticides, at relatively low concentrations.

EXAMPLES

Experimental Section

Most of the experiments were carried out using multi-walled carbon nanotubes (MWNTs), referred to as CNTs. They were dispersed in water (2 mg in 25 mL water) using sodium dodecyl sulfate (6 mg) as a surfactant [K. Moshhammer, F. Hennrich, M. M. Kappes, *Nano Res.* 2009, 2, 599-606]. This CNT suspension was drop cast onto Whatman 42 filter paper (3 μ L of the CNT suspension coating 5 mm²). Then the paper was dried in air and cut into triangles with dimensions 2 \times 5 mm (base \times height). The CNT-coated paper triangle was connected to a 3 V battery and held close (2 mm) to the mass spectrometer inlet. Then it was loaded with sample (typically as 30 ppm solutions). The volume of solvent used was 2

μL and repeated measurements using the same paper used the same aliquot of pure solvent. All measurements were made at 3 V. Mass spectra were recorded in the positive ion mode for all analytes except preformed ions. For preformed ions derived from salts, both positive and negative ion mode spectra were recorded at $\pm 3\text{V}$. All spectra were recorded under the following experimental conditions: solvent methanol/water (1:1), source voltage $\pm 3\text{V}$, capillary temperature 150°C , capillary voltage $\pm 15\text{ V}$, and tube lens voltage $\pm 55\text{ V}$. Single walled carbon nanotubes (SWNTs) were also used for the measurements but no detectable enhancement in signal was seen. Following parameters were used for all the ESI experiments: Source voltage -5 kV , sheath gas (nitrogen) flow rate 8 (manufacturer's unit), solvent flow rate $2\mu\text{L}/\text{min}$ and all other parameters were same as paper spray. All ESI mass spectra correspond to an average of 100 scans. SWCNTs and MWCNTs were purchased from Nanocyl s.a, USA; SDS from RFCL Ltd., Gujarat, India; TPP from Spectrochem Pvt. Ltd., Mumbai, India; tributylphosphine from Wako Pure Chemical Industries Ltd.; diphenylamine and triethylamine from Merck Ltd., Mumbai, India. The pesticides, carbofuran, methyl parathion and parathion, were purchased from Sigma Aldrich, India. All the medical tablets used (Crocic, Combiflam and Xyzal, all trade names) were purchased from a local pharmacy. Amino acids used in the experiments were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. All analytes (other than pesticides and tablets) were used at 30 ppm concentration. HPLC grade methanol (Sigma Aldrich) and MeOH/water 1:1 were used as solvents. All mass spectra were recorded using an ion trap LTQ XL (Thermo Scientific, San Jose, CA). MS^2 analysis using collision-induced dissociation was performed to confirm the identity of the ions. Raman measurements were made using a Witec GmbH Confocal Raman Microspectrometer, Germany with 532 nm and 633 nm laser excitations. A FEI make field emission SEM was used to image the CNT-coated paper samples.

A CNT-impregnated paper is used to generate ions from organic molecules at potentials as low as 3 V. Common pesticides from the surface of an orange, ingredients of medicinal tablets and a variety of analytes such as amino acids have been characterized by this method.

It may be appreciated by those skilled in the art that the drawings, examples and detailed description herein are to be regarded in an illustrative rather than a restrictive manner.

We Claim:

CLEAN COPY

1. An ionization source to generate ions from organic molecules under low electric potentials in mass spectrometry, wherein the said ionization source is prepared from a paper impregnated or coated with nanometer-sized CNTs which generate ions at potentials as low as 3 V.
2. The ionization source as claimed in claim 1, wherein the nanometer-sized CNTs at the modified paper surface are responsible for high electric fields.
3. The ionization source as claimed in claim 1, wherein the ionization is achieved at potentials as low as 3V derived from a battery
4. The ionization source as claimed in claim 1, wherein the nanometer-sized CNTs coated paper produces molecular ionization.
5. The ionization source as claimed in claim 1, wherein the ionization source generates and analyses ions from a variety of compounds including organic compounds, pesticides, ingredients of medicinal tablets and amino acids.
6. The ionization source as claimed in claim 1, wherein the nanometer-sized CNTs coated paper is shaped as triangles, squares or rectangles.
7. The ionization source as claimed in claim 1, wherein the paper coated with CNTs is made from the group including cellulose, polymers and leather.
8. The ionization source as claimed in claim 1, wherein the nanoscale feature is selected from nanoscale object including nanorods, nanotubes, nanosheets, nanotriangles and nanoflowers.

Dated at Chennai this June 01, 2019

Signature: 

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA - 369

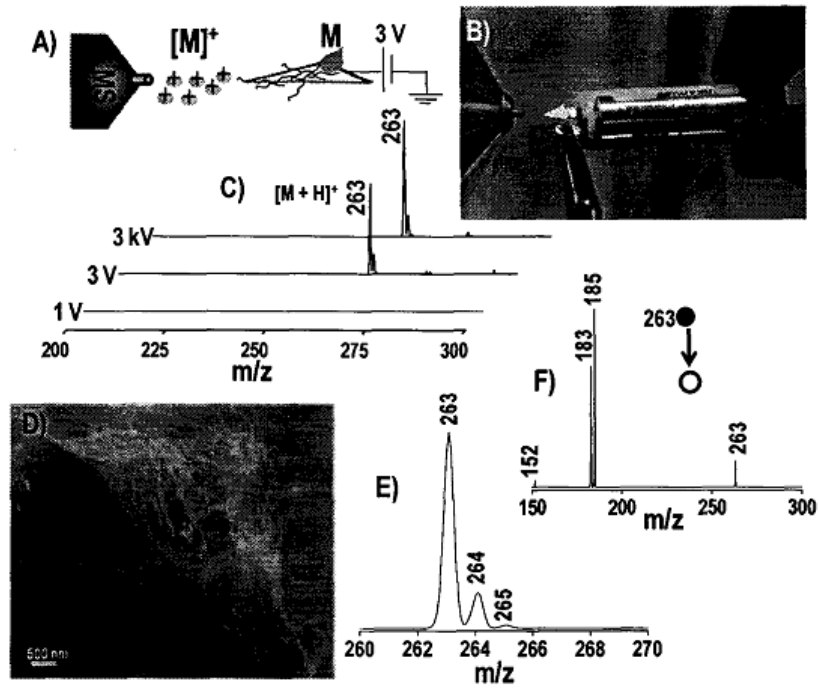
MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER FIELD OF THE INVENTION

Abstract

The present invention relates to ambient ionization from impregnated / coated paper source for mass spectrometry and methods thereof. The said impregnations / coatings are achieved using carbon nanotubes (CNTs). The CNT-impregnated paper is used to generate ions from organic molecules at potentials as low as 3V. Further the present invention demonstrates the possibility of analytical mass spectrometry with a battery.

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 1

15

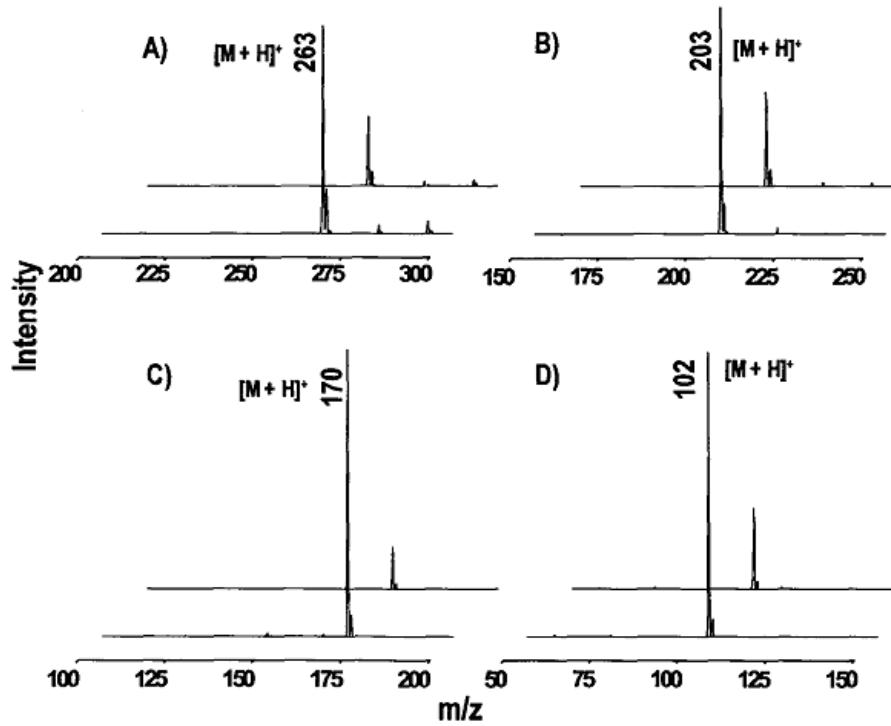
20

Signature:

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 2

15

Signature: 

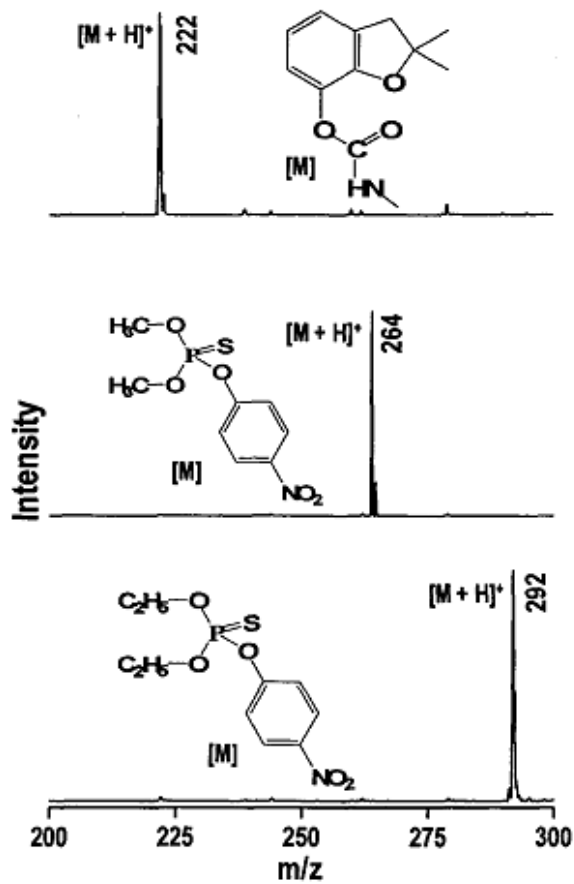
20

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 3

15

Signature: 

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

20

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5

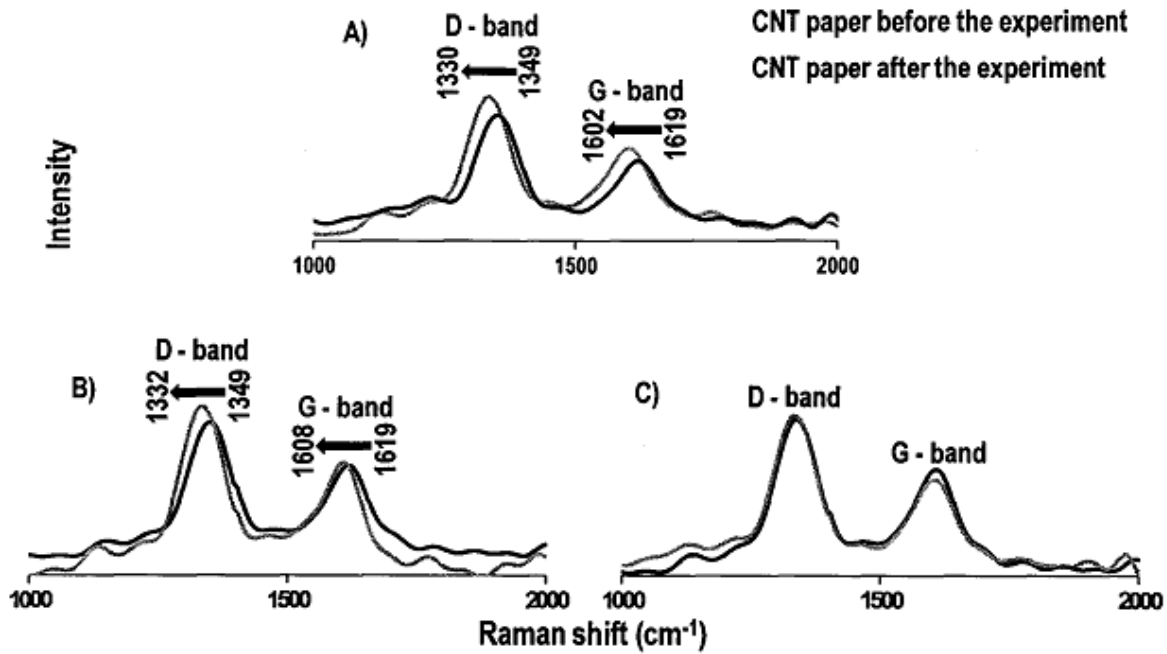


FIGURE 4

10

Signature: 

15

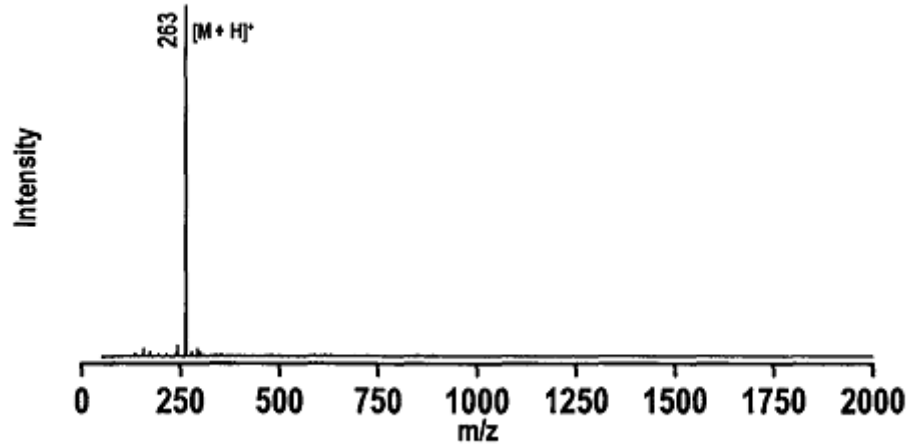
D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

20

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 5

15

Signature: 

20

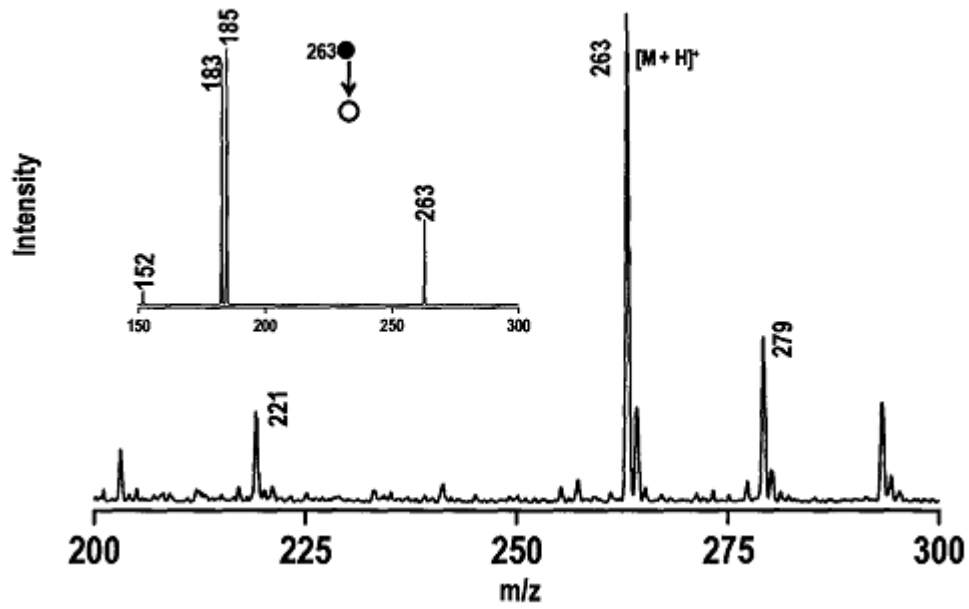
D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

25

30

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 6

15

Signature:

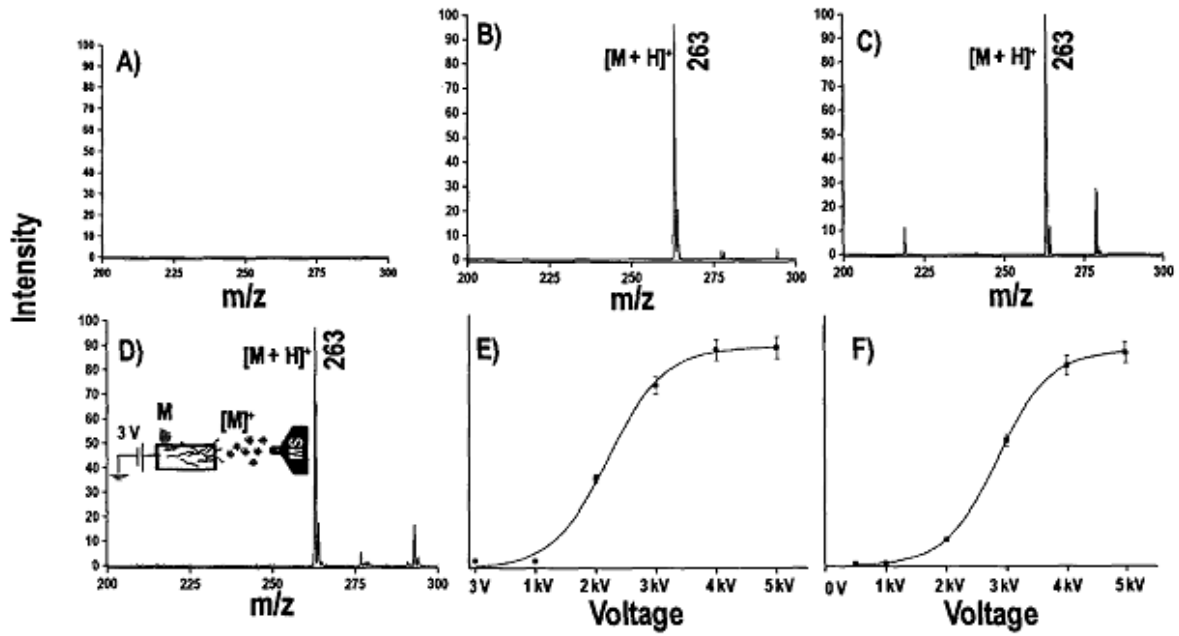
20

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 7

15

Signature:

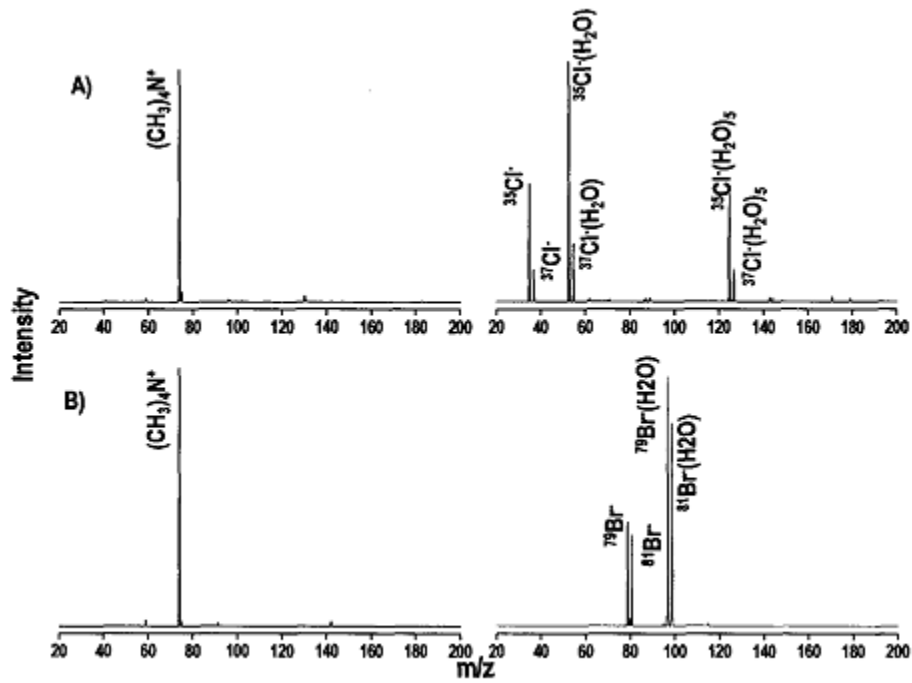
D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

20

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 8

15

Signature:

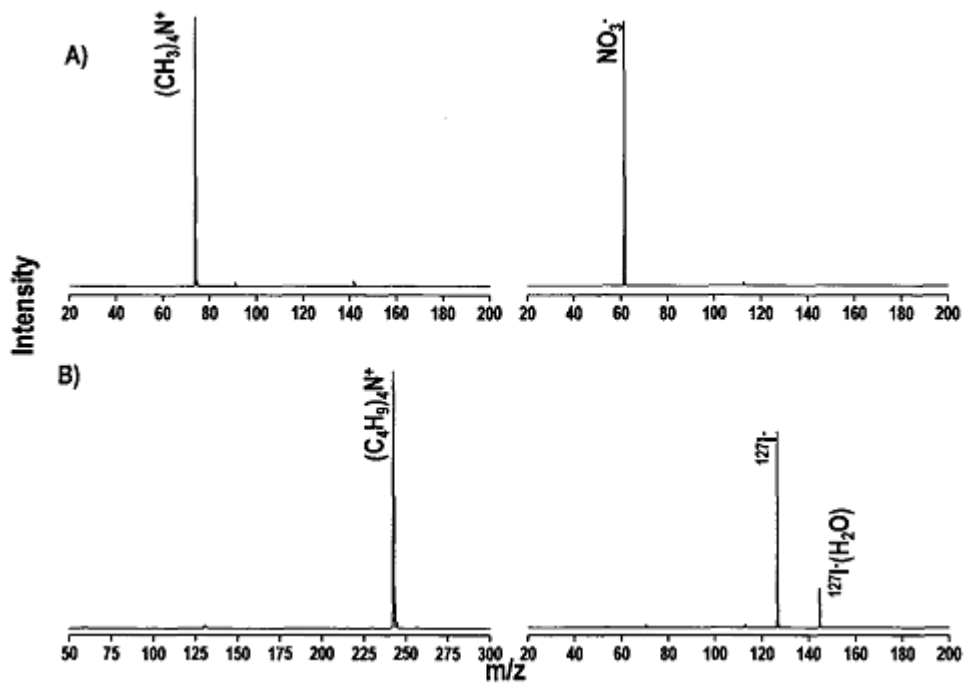
D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

20

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 9

15

20

Signature:

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

25

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5

10

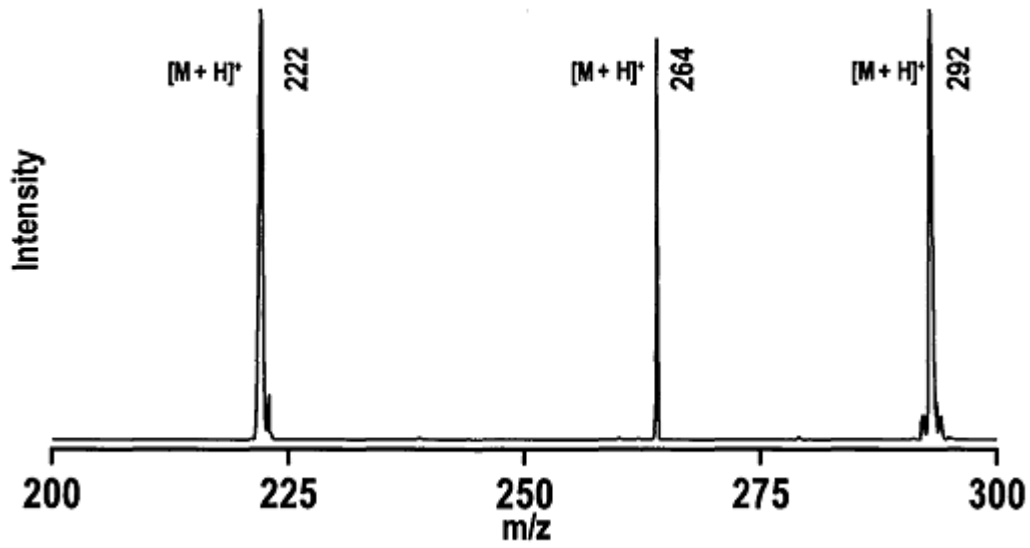


FIGURE 10

15

20

Signature: 

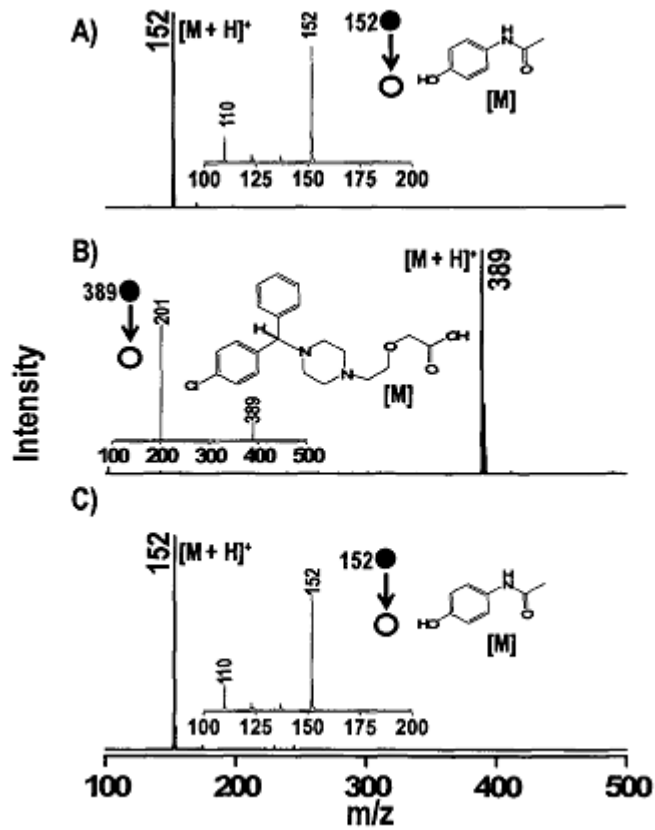
D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

25

30

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5



10

FIGURE 11

15

Signature:

D. Moses Jeyakaran
 Advocate & Patent Agent
 IN/PA — 369

20

MOLECULAR IONIZATION FROM CARBON NANOTUBE PAPER

5

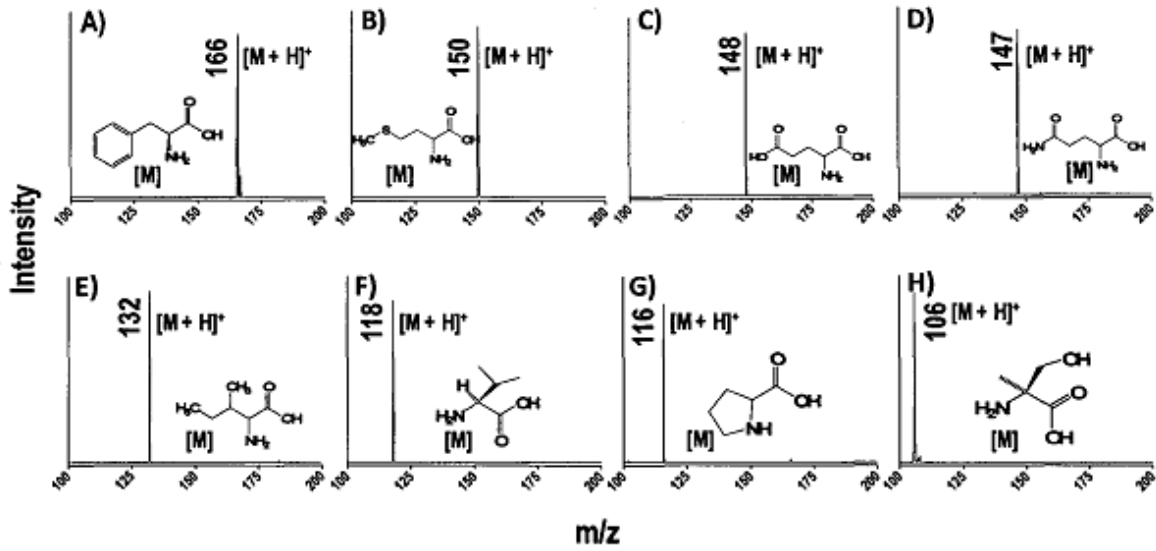


FIGURE 12

10

Signature:

15

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

20

25