

Nicotinic acid as Matrix of elements

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Abstract: In This research work, an arrangement of the laser ionization mass analyzer was used to study nicotinic acid. The elements were found from the nicotinic acid spectrum, the nicotinic acid attached to Li^7 , V^{51} and Fe^{57} .

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In laser ionization mass spectrometry, since only laser is used for both vaporization and ionization, the technique is very simple. This factor may provide the easiest or best route to an understanding of the laser / solid interaction⁷.

Instrumentation

He- Ne laser is a pulse mode (Leybold Didactic), ideal for time of flight mass spectrometry, provides a laser radiation at a wavelength of 337nm with a maximum energy per laser pulse (full width at half max 4 to 5 ns) of 1.2 mJ. The laser has a maximum power output of 300 kW. The laser was triggered externally by a pulse generator operated at 10 Hz, figure (1): This figure shows a vacuum system, mass analysis system, power unit, capable of delivering voltages between 0-3 kv.

Positive ions formed at the repeller at the high positive potential, +1 kv are accelerated towards the extraction cone receiving 1 keV of kinetic – energy pass through the 1mm diameter hole in the center of the extraction cone. The einzel lens assembly was separated from the extraction cone by a layer of insulating material. The function of the lens was to distort the path of the ions slightly so they were brought to a "focus" in the plane of the detector at the same time. It was kept at a high positive potential during this project, (usually between 20% less than the repeller potential).

Introduction

Lasers are increasingly used in chemistry for synthetic, spectroscopic and analytical purposes. In particular, the combination of lasers and mass spectrometry is a surprisingly broad subject, ranging from the multi -photon ionization of gas phase organic molecules capable of detecting single molecules to laser desorption mass spectrometry, which uses low power laser irradiation of surfaces to produce molecular ions with a minimum of fragmentation¹.

Laser microprobe mass spectrometry can be used to analyze bulk solids and near surface layers². The technique is multidisciplinary in many senses because it is applicable to the analysis of any vacuum compatible solid, and its development has meant the fusion of a number of advanced but quite disparate technologies.

The Laser microprobe mass spectrometry technique uses a single laser to excite solid targets and to generate ions. The ions are separated according to their mass – to – charge ratio in a time of flight mass spectrometer. This type of spectrometer is ideally suited to the instantaneous production of ions from a pulsed source. It collects all the ions from a single event and is thus very sensitive³⁻⁶.

The use of an assembly system type instrument to investigate laser vaporization and ionization of solids, and the use of the technique as an analytical tool is discussed.

distortions in a supposedly linearly increasing electric field. This occurred at the entrance to the reflectron (on ground) and at the deepest end of the reflectron. This problem was solved by spot welding stretched copper grids across the two entrance elements and the end element. These grids provided a complete plane at a single potential through which equi-potential lines from elsewhere could not penetrate, rather than just a ring at a single potential. The grids had enough transmission not to significantly reduce the ion signal received at the detector.

The purpose of this is to amplify the current produced by ion packets arriving at the detector at different times, after passing through the field-free region and the reflectron. The front of the plates is covered with a grid at ground. To preserve the field-free drift region. After passing this the ions experience a strong acceleration towards the first micro channel plate. A "shower" of electrons is produced. These are accelerated towards the second plate where the signal is amplified i.e. the number of electrons is increased by two to three orders of magnitude. These electrons then hit the anode and the current produced, converted to a voltage, registers on the oscilloscope trace. The micro channel plates are circular with 2 cm diameter with a central hole of 4mm diameter. They are mounted on the reverse side of the extraction core. This is illustrated in figure (1).

Insulated from the einzel lens is the central passage into the field free drift region of the mass spectrometer where the ions are affected by no electric fields until they enter the reflectron. The central passage is at ground potential. Assuming that all the energy have been supplied to the particle when acceleration is in the form of translational kinetic energy.

Hence light move faster through the field free-region than do equally charged heavy particle. This is the basis of the production of a mass spectrum from the different flight times of different masses of ions through a set distance.

A linear type reflectron with cylindrical geometry is used the novel feature of this reflectron is the shape of the elements used: these are rings with a steep step in them to shield the ion reflecting volume from field in homogeneities due to edge effects at the ends of elements and also to shield from any insulators present that could charge up and cause field distortion. The voltages between each step were controlled by a series of resistors of equal value of 330kΩ acting as a potential divider. A high positive potential roughly 20% greater than that applied to the repeller is applied across the reflectron elements. The rings would suffice as reflecting elements but after various simulations it was found that the field produced by one element could penetrate into the next ring, leading to severe

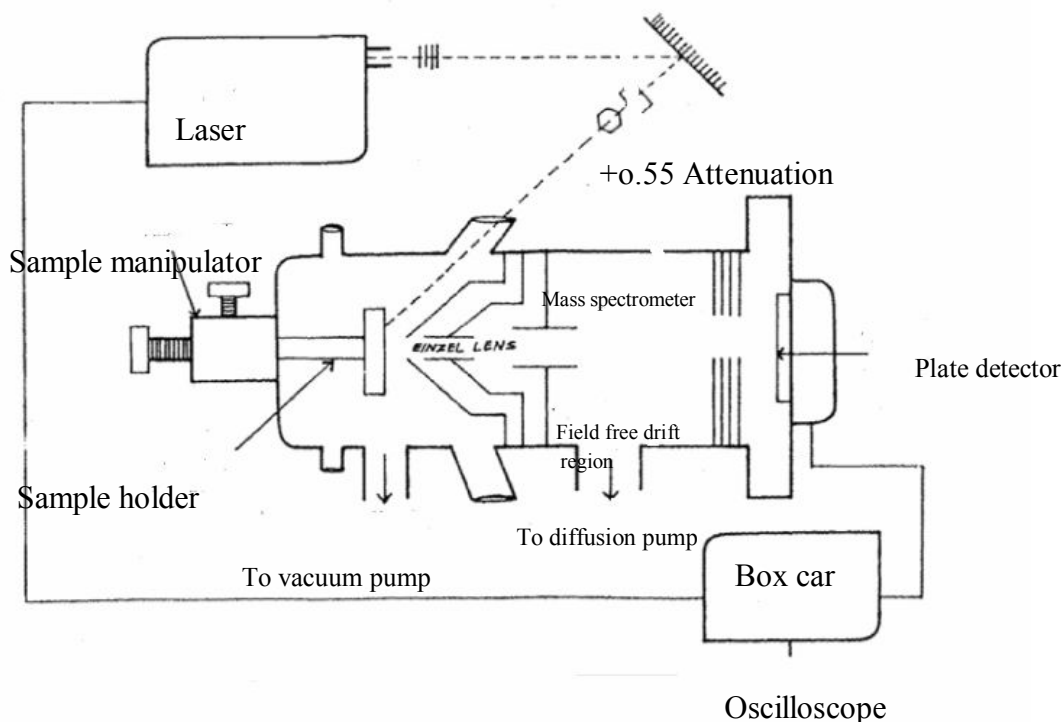


Fig.1. The Laser Ionization Mass Analyzer instruments.

ions is known we can use this equation to find out the mass by applying the above equation. Its derivation follows:

For two ions of masses m_1 and m_2 , arriving at times t_1 and t_2 the ions travel through the drift region of length, s , at this constant velocity v , q is the charge, on the particle in coulombs. E.K. is kinetic energy. m , is mass of the particle in kg and v is the velocity of particle.

From primary equations

$$E = qv \dots (a) \text{ and } E.K = \frac{1}{2}mv^2 \dots (b) \text{ \& } t = \frac{s}{v} (c)$$

From equations (a), (b) and (c), we obtain,

$$t^2 = \left(\frac{s^2}{2Ek} \right) m \text{ where; } w \text{ is potential energy in joules.}$$

Hence a graph of t^2 against m should be a straight line of slope $s^2/2Ek$. If a straight line is obtained, then eq. $m_2 = m_1(t_2/t_1)^2$ can be applied to all mass ranges, but if it varies then will only be applicable over smaller mass ranges.

The material to be studied was placed in the sample holder prior to pumping the whole system to near vacuum. The sample size was not considered to be important, since the analysis was qualitative and not quantitative. For nicotinic acid a small quantity was placed on the sample holder, dries with hair dryer before it was placed back. He – Ne laser energy output was obtained. When the flow – meter was adjusted to between 15-20%, with a pressure of 100 mbar, voltage of 15 kv, and a repetition rate of 10 Hz. The mass intensity peaks were then displayed in the digital oscilloscope on the Y-axis and the arrival times of the ions in μs at the detector on the X- axis. The laser pulse and atomic signal at the detector were synchronized. The start of the laser pulse was shown as zero μs on the X-axis^{8,9}.

Mathematical method

Calculation of mass from the spectrum was carried out using the equation: $m_2 = m_1(t_2 / t_1)^2$

Where, m_1 and t_1 are the mass and arrival time of the first ion and m_2 and t_2 are the mass and arrival time of the second ion. Since the time of arrivals of

Table(1): arrival times in μs at the detector, calculated masses, and possible elements for Nicotinic acid.

<i>T</i> (μs)	<i>Mass</i>	<i>Possible element</i>
9.72	22.9897	<i>Na</i> ²³
10.52	26.9297	<i>Al</i> ²³
10.72	27.9634	<i>Si</i> ²⁸
12.64	38.8772	<i>k</i> ³⁹
14.32	49.8984	<i>Ti</i> ⁵⁰ , <i>V</i> ⁵⁰ , <i>Cr</i> ⁵⁰
14.32	50.8788	<i>V</i> ⁵¹
14.60	51.8688	<i>Cr</i> ⁵²
15.00	54.7499	<i>Mn</i> ⁵⁵
15.14	55.7766	<i>Fe</i> ⁵⁶
15.40	57.7088	<i>Fe</i> ⁵⁸ , <i>Ni</i> ⁵⁸
15.66	59.6748	<i>Ni</i> ⁶⁰
16.68	67.7006	<i>Zn</i> ⁶⁸
16.80	68.6782	<i>Ca</i> ⁶⁹
17.88	77.7921	<i>Se</i> ⁷⁸
18.12	79.8945	<i>Se</i> ⁸⁰ , <i>Kr</i> ⁸⁰
20.84	105.6807	<i>pd</i> ¹⁰⁶ , <i>cd</i> ¹⁰⁶
22.56	123.8451	<i>Nicotinc Acid</i> , <i>Sn</i> ¹²⁴ , <i>Te</i> ¹²⁴
23.16	130.5202	<i>NicotinicAcid</i> + <i>Li</i> ⁷
26.76	174.25	<i>NicotinicAcid</i> + <i>V</i> ⁵¹
27.24	180.5572	<i>NicotinicAcid</i> + <i>Fe</i> ⁵⁷

The instrument also proves to be sensitive, as be seen from the mass spectra, a number of elements were identified. These elements were constituents of the samples analyzed. There were peaks due to a trace of contamination from fingers during handling of samples such as Na, K, or constituents of sample holder. Also we can conclude that some of the fragments of nicotinic acid appear in the spectrums¹⁰.

The efficiency of laser ionizations and ion yields depend largely on power intensity, these condition can be achieved using the described laser ionization mass analyzer instrument by tuning and focusing the laser. Quantitative analysis will be an obstacle using this instrument, because as it is well known that the laser – solid interaction is not adequately comprehensive. This laser ionization mass analyzer instrument uses one laser for both evaporation and ionization. Hence, it can not be used for quantitative analysis. Many attempts have been carried out, to combine the processes of evaporation and ionization, with the aims of trying to make the composition of the vapor phase directly proportional to the constituents of the sample. By improving the efficiency of ionization of evaporated sample the ion yield will directly be proportional to the concentration.

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Results

The mass intensity peaks were displayed in the digital oscilloscope on the Y-axis and the arrival times in μs of the detector on X-axis. Given the arrival times from the spectrum the determinations of unknown masses of the ions were calculated using the above equation. The results are shown in table (1) for nicotinic acid. Table(1): possible elements, calculated masses

Conclusion

In the nicotinic acid spectrum, the prominent peak at $T=22.56\mu\text{s}$ was of the nicotinic acid molecule, the next one at $T=23.16\mu\text{s}$ was due to nicotinic acid attached to Li^7 ion, the peak at $T=26.76\mu\text{s}$ was due to the attachment of the nicotinic acid with V^{51} ion. And the last peak at $T=27.24\mu\text{s}$, was due to nicotinic acid attachment to Fe^{57} ion. There was a prominent peak at $T=17.88\mu\text{s}$, this was probably due to the nicotinic acid ring (pyridine), in this case the nicotinic acid molecule was fragmented by what is known as hard ionization into the functional carboxyl group COOH and the pyridine group.

The method has proved to be adequate, and masses obtained were consistent with the real values.

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