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Photoelectron Emission as an Alternative Electron Impact Ionization Source for Ion Trap Mass Spectrometry

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Electron impact ionization has several known advantages; however, heated filament electron sources have pressure limitations and their power consumption can be significant for certain applications, such as in field-portable instruments. Herein, we evaluate a VUV krypton lamp as an alternative source for ionization inside the ion trap of a mass spectrometer. The observed fragmentation patterns are more characteristic of electron impact ionization than photoionization. In addition, mass spectra of analytes with ionization potentials higher than the lamp's photon energy (10.6 eV) can be easily obtained. A photoelectron impact ionization mechanism is suggested by the observed data allowed by the work function of the ion trap electrodes (4.5 eV), which is well within the lamp's photon energy. In this case, the photoelectrons emitted at the surface of the ion trap end-cap electrode are accelerated by the applied rf field to the ring electrode. This allows the photoelectrons to gain sufficient energy to ionize compounds with high ionization potentials to yield mass spectra characteristic of electron impact. In this manner, electron impact ionization can be used in ion trap mass spectrometers at low powers and without the limitations imposed by elevated pressures on heated filaments.

Electron impact ionization (EI) is one of the most widely used techniques in mass spectrometry. Its applicability includes all types of atoms and compounds, the resulting characteristic mass spectra do not depend as much on instrumental parameters compared to other ionization techniques, and spectral databases are widely available. These advantages make EI ideal for characterization of unknowns.

Typically, heated filaments are used as a source of electrons in electron impact ionization because of their simplicity. However, they can only be operated below certain pressures because the filament lifetime decreases dramatically at higher pressures, particularly when the background gas is air.¹ This represents a limit for its applicability to ion trap mass spectrometers (ITMS) that are operated at higher pressures; for example, in miniature ITMS instruments operation in the milli Torr range is possible.²

In addition, the power consumption of heated filaments can also become a limitation in field-portable instruments.¹ Thus, low-cost and low-power consumption electron sources are needed, which can also be operated at high pressures.

Recently, we have reported the design and construction of an ion trap/time-of-flight (IT/TOF) mass spectrometer.³ Its main purpose is to serve as a detector for high spatial resolution analysis of surfaces via near-field laser ablation sampling.⁴ In essence, the neutrals from the ablation plume are sampled and directed to the ion trap via a differentially pumped interface. A heated filament EI source is used to perform ionization of the ions from the transient plume, which are "preconcentrated" in the trap, and then extracted to the TOF MS. One of the main limitations in this experiment is the low amount of sample that makes it to the ion trap. The amount of neutral analyte gas transported to the IT can be improved by allowing an overall higher amount of gas to make it to the ion trap; however, this will lead to a pressure increase in the IT stage. Thus, an alternative in-trap ionization source is also required for our purpose.

Laser-induced electron emission has been previously used as an alternative source of electrons exclusively for EI TOF MS^{5–13} and electron attachment TOF MS.^{14–16} Basically, a laser beam is directed to a metal surface whose work function lies below the photon energy. The resulting photoelectrons can then be accelerated to a desired energy. An advantage of photoelectron sources in comparison to heated filaments is the ability to work at a wider pressure range. This characteristic suits our previously mentioned

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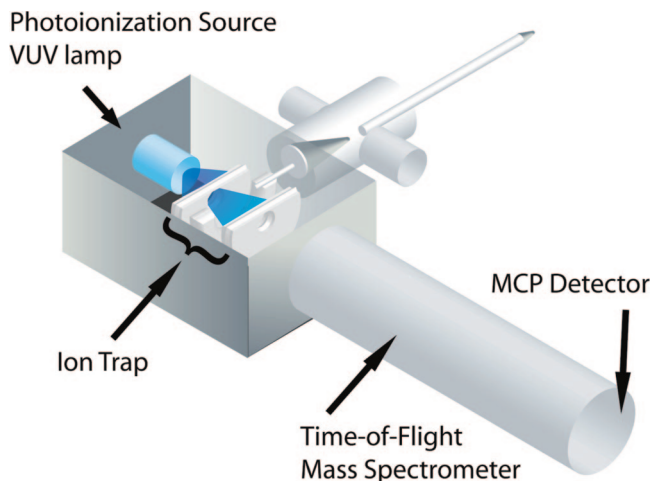


Figure 1. Schematic of the in-trap ionization setup of the IT/TOF MS. The VUV krypton lamp was replaced by a heated filament electron gun for selected experiments.

experimental requirements and could prove to be useful for miniature ITMS applications, such as portable mass spectrometers.

We report herein on the use of a VUV krypton lamp as an alternative electron source for in-trap electron impact ionization in an IT/TOF mass spectrometer described previously.³ The fragmentation patterns and ionization of compounds with ionization potentials higher than the photon energy suggests that photoelectron impact ionization is the major channel. In addition, the limits of detection of selected compounds are evaluated and compared to a heated filament EI source.

EXPERIMENTAL SECTION

Reagents. All compounds were higher than 99% purity unless otherwise stated. Toluene, *p*-xylene, and bromobenzene were purchased from Fluka (Buchs, Switzerland). Dichloromethane and chloroform were purchased from Mallinckrodt Baker (Griesheim, Germany). *n*-Hexane, HPLC grade, was purchased from Scharlau (Barcelona, Spain). All gases (argon, 99.998%; neon, 99.995%; carbon dioxide, 99.9%) were purchased from PanGas (Dagmersellen, Switzerland).

Instrumentation. Figure 1 shows a schematic diagram of the IT/TOF MS and the position of the VUV lamp ionization source. The instrument has been described in detail previously;³ however, there are some modifications worth mentioning. The previous double-skimmer arrangement has been replaced by a single-skimmer setup. A passivated stainless steel tube is fitted to the back of the skimmer and goes through the side of the ring electrode (not between the ring electrode and the end cap electrode as described in ref 3) such that the sample is delivered inside of the ion trap. The heated filament EI source is placed behind the end cap of the IT, which also serves as the repeller during extraction for the TOF MS. For the present study, the heated filament was replaced by a VUV krypton lamp (PKS 106, Heraeus Noblelight GmbH, Hanau, Germany) powered by a high-voltage power supply (HCN 140–3500, FuG Elektronik GmbH, Rosenheim, Germany) through an 8-M Ω resistor. An in-house-built voltage pulser was used in certain experiments where the lamp was pulsed for 20 ms and the resulting ions were trapped for a few extra milliseconds (1–5 ms) followed by extraction to the TOF MS (mass resolution of 297 at m/z 104).³

Methods. For the first set of experiments, the analyte gas or vapor was delivered to the sampling capillary such that there was sufficient signal to observe the fragmentation pattern or the ionization potential dependence. A total of 20 spectra/sample were averaged on the digital oscilloscope. The limits of detection (LODs) were determined by an exponential dilution method.^{17–20} In this technique, an exponential dilution chamber is used to introduce a continuously decreasing and known concentration of analyte into the mass spectrometer. The exponential dilution chamber consisted of a triple-neck round-bottom flask where the first neck was coupled to the MS sampling capillary, the middle-neck was stoppered with a septum, and the last neck was connected to a Teflon tube, which was open to the air. The airflow through the dilution chamber (volume 91 mL) was 65 mL/min from the sampling capillary suction. Analyte vapor (10–50 μ L) was injected through the septum, and adequate mixing was ensured through a magnetic stirring bar. The sample concentration as a function of time (C_t) was obtained according to $C_t = C_0 \exp(-Ut/V)$ from the flow rate (U), dilution cell volume (V), and the sample's vapor pressure.^{18–20} The mass spectra collection rate was kept at 10 Hz, and a LabView virtual instrument (LabVIEW 7.1, National Instruments, Austin, TX) was written to transfer the spectra from the digital oscilloscope to a computer and yield the m/z peak areas as a function of time.

RESULTS AND DISCUSSION

A series of experiments were performed to determine the ionization characteristics of the krypton lamp source. First, several compound vapors and gases were introduced into the mass spectrometer to study the fragmentation patterns and signal intensities. For most of these experiments, the krypton lamp was operated continuously (always on). Figure 2A shows the IT/TOF mass spectra of toluene with the VUV krypton lamp ionization. The krypton lamp ionization mass spectra is dominated by the peak at 91 m/z . Unfortunately, due to the resolution of the instrument, the peak at 92 m/z only shows as a shoulder on the 91 m/z peak. In photoionization, the peak at 92 m/z should be the dominant one, so this is the first indication that a harder ionization is actually taking place.^{21,22} The peak at 65 m/z is a toluene fragment. This is another indication of harder ionization. An evident feature of the spectrum is the high background due to the continuous operation of the krypton lamp, which results in the constant generation of ions during the extraction pulse. This will be discussed below. Figure 2B shows the characteristic mass spectrum obtained with an EI filament source. In this case, the EI filament source is gated such that ionization only takes place in a 5-ms window starting 15 ms before the extraction pulse. Thus, the background due to the constant ionization is not present. Figure 2C gives a NIST EI toluene mass spectra for reference.²³ It seems that the VUV lamp source spectra of toluene is more

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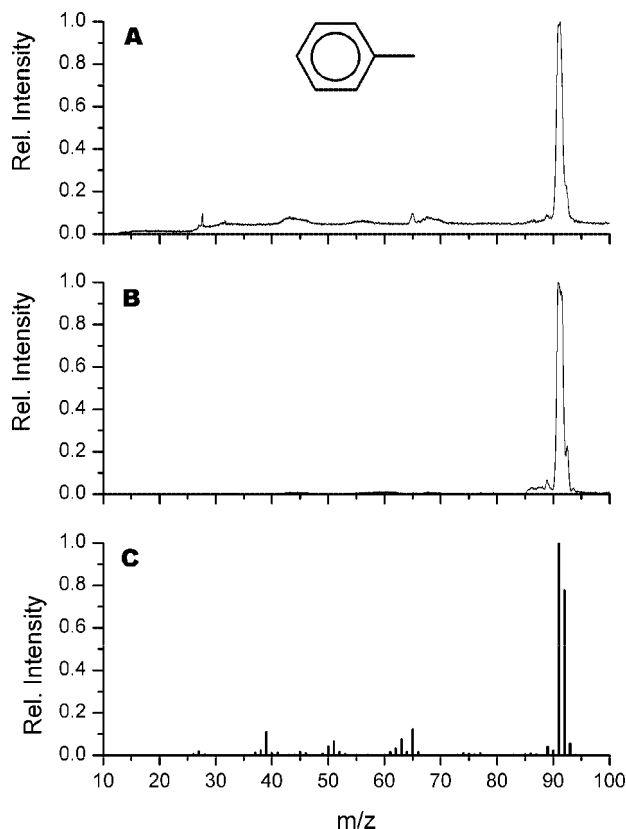


Figure 2. Mass spectra of toluene with VUV krypton lamp (A), gated heated filament electron gun (B), and electron impact reference spectra from NIST (C). Similarities on all three spectra are apparent.

characteristic of EI spectra than PI spectra,^{21,22} which was also the case for hexane, *p*-xylene, and bromobenzene (data not shown). Next, compounds with higher ionization potentials than the photon energy of the krypton lamp (10.6 eV) were tested. Figure 3 shows the IT/TOF mass spectra of chloroform (IP 11.4 eV) with the VUV krypton lamp source (A), EI filament (B), and EI NIST ref 23 (C). Under normal circumstances, the VUV lamp should not be able to ionize the chloroform, but we could easily obtain mass spectra. In addition, one does not have to compare the different spectra very closely to see that the VUV lamp spectrum is very similar to the EI spectra. Dichloromethane was also investigated and yielded similar results (data not shown).

Several gases with increasing ionization potentials were also tested to characterize the limits of this approach with the VUV krypton source. Figure 4 shows the krypton lamp source IT/TOF mass spectra when carbon dioxide (IP 13.8 eV, Figure 3A), argon (IP 15.8 eV, Figure 3B), or neon (IP 21.5 eV, Figure 3C) is sampled. In the case of carbon dioxide and argon, the VUV lamp was operated continuously. In the case of neon, however, the signal is not very high so the VUV lamp is operated in pulsed mode to decrease the background. In each corresponding spectrum, the carbon dioxide peak at *m/z* 44, argon at *m/z* 40, and neon at *m/z* 20 are evident. Also, major peaks at *m/z* 32 and 28, which correspond to oxygen (IP 12.1 eV) and nitrogen (IP 15.6 eV), can be observed. In the experiments where the VUV lamp is operated continuously, the major component of the sampled gas, carbon dioxide or argon, dictates at which *m/z* the background appears (Figure 4A,B). It is also clear this is no longer

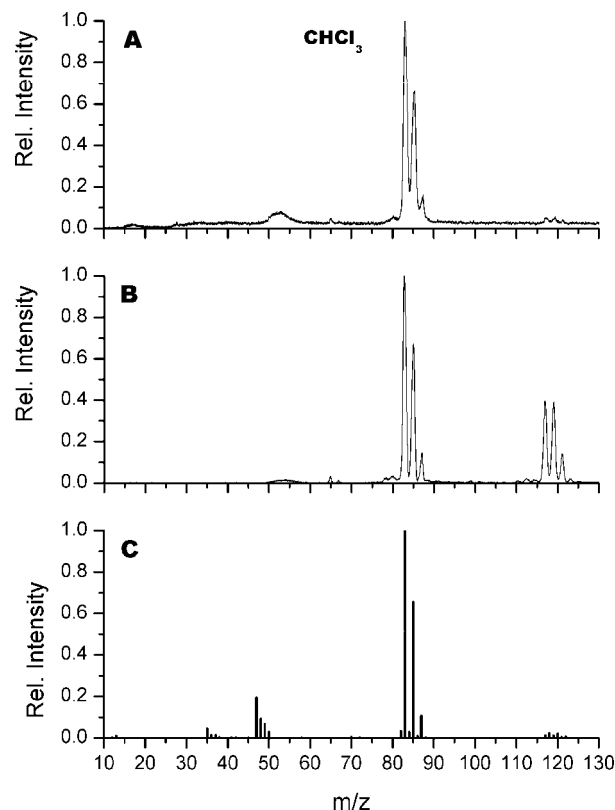


Figure 3. Mass spectra of chloroform with VUV krypton lamp (A), gated heated filament electron gun (B), and electron impact reference spectra from NIST (C). Fragmentation characteristics are very similar for all three spectra.

the case when the lamp is pulsed (Figure 4C). The small signal of neon compared to argon or carbon dioxide could be due to several factors. One is lower concentration because for these experiments no effort was taken to deliver pure gas into the mass spectrometer. Instead, the gas was guided to the entrance of the sampling capillary where it had a chance to mix with air, which explains the observed peaks for oxygen and nitrogen. Neon has a higher diffusion efficiency compared to argon and carbon dioxide, which would decrease its concentration at the sampling point. Another factor that could play an important role is the trapping efficiency, which in our setup decreases noticeably below 30 *m/z*. The possible effect of the high IP of neon will be further discussed below.

As stated earlier, the energy of the photons coming from the krypton lamp is sufficient to ionize substances with an ionization potential below 10.6 eV via single photon photoionization. For compounds with ionization potentials higher than 10.6 eV, a multiphoton scenario is highly unlikely because the source is not coherent and its irradiance is not very high. One possibility concerning the molecular compounds is that the ions from photoionization have enough internal energy to yield fragment ions.²⁴ Photoionization efficiency curves (efficiency vs photon energy) obtained via time-resolved photoionization mass spectrometry have shown, for example, that for toluene-*d*₈ the appearance energy of fragment ions is lowered by increasing the time

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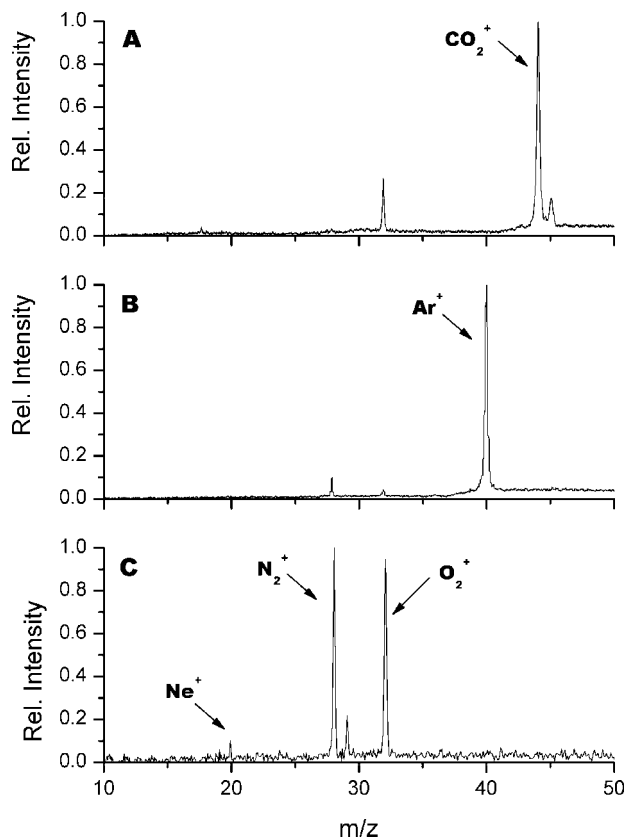


Figure 4. Mass spectra obtained with VUV krypton lamp while carbon dioxide (A), argon (B), and neon (C) were sampled. It is evident that the lamp is able to ionize analytes with much higher IP than the photon energy.

molecular ions spend in an ion trap.^{24,25} The appearance energy shift, however, is not high enough to give the fragmentation patterns observed in the present study.²⁵ On the other hand, the similarity of the fragmentation patterns between the EI and the krypton lamp mass spectra suggests an electron impact ionization mechanism. Thermal electron emission can be ruled out since the surfaces remain at room temperature. The most straightforward explanation then is photoelectron emission. The work function of the ion trap electrodes, which are made of stainless steel, ~ 4.5 eV, is well within the energy of the emitted photons from the krypton lamp. Thus, this would be the most likely source of electrons for EI. To study this phenomenon, the current on each electrode of the ion trap was measured as a function of the krypton lamp applied current while no external voltages were applied to the ion trap (coaxial cables disconnected; Figure 5). It is evident that there is no current on any electrode when the krypton lamp is off. When the lamp is on, however, the repeller/end-cap electrode is characterized by having the highest positive current because most of the light from the lamp illuminates this electrode. However, the light hits the outside surface of the repeller/end-cap electrode; thus, most of these photoelectrons will not participate in in-trap ionization. The current is positive because electrons are being ejected from the electrode. Some of the photons from the lamp can go through the hole in the center of the repeller/end cap and impinge on the inner surface of the

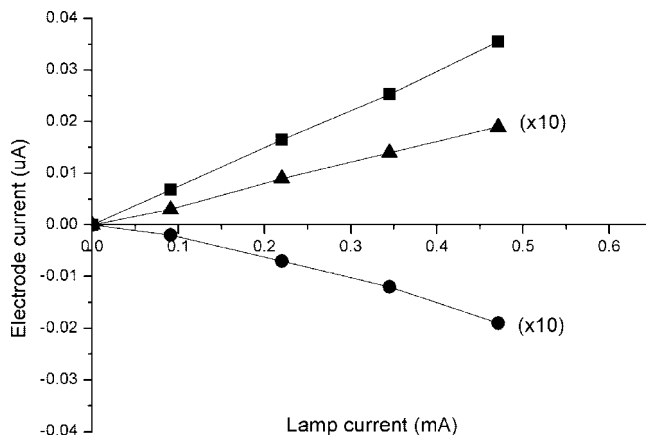


Figure 5. Measured current on the repeller/end cap (■), extractor/end cap (▲), and ring (●) electrodes as a function of applied VUV lamp current in the absence of any applied voltage to the ion trap.

extractor/end cap, which will also result in a positive current albeit smaller than on the repeller. No photons can hit the ring electrode directly due to the geometry of the setup; thus, only negative current can be measured from electrons generated elsewhere that hit the electrode's surface. If the lamp is considered a point source, then it would illuminate a circle of 10.7-mm diameter on the center of the extractor. The extractor, however, has a hole of 3.5-mm i.d. in the center; thus, not all of the area will be available for photoelectron emission. The current on all electrodes increases virtually linearly with the lamp's applied current. Also, the extractor and ring electrode have very similar current values, which may be an indication that most of the electrons inside the trap come from the extractor electrode.

At the point where the photoelectrons are ejected, they can have an excess energy ranging from zero to the difference between the energy of the impinging photon and the surface work function. In addition, the electrons can be accelerated by the applied rf voltage during the positive half-cycle. The average value of half a cycle of a sine wave is given by $2A\pi^{-1}$, where A is the peak amplitude. In our measurements, we used rf potentials ranging from 360 to 900 V_{pp} ; thus, the electrons were subjected to peak potentials from 180 to 450 V and average potentials from 115 to 287 V during the positive cycles. Going back to the neon signal discussion, this energy is more than enough to ionize neon and in fact give close to optimum electron impact ionization cross sections for neon; thus, the high IP of neon should not play a significant role in the low signal observed.²⁶ This is also the case for the other compounds studied.^{26–28}

Finally, the LODs for a few selected compounds were determined via heated filament EI and the VUV krypton lamp (Table 1). It is important to note that the sources were gated/pulsed-on for only 20 ms/mass spectrum. The original purpose of the study was to explore alternative ionization sources for an IT/TOFMS coupled to near-field laser ablation sampling, and the 20 ms corresponds to the temporal spread of the transient laser ablation plume. Thus, no efforts were made to improve the limits of detection by increasing the ionization time. It is apparent from

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Table 1. Limits of Detection (ppm) of Selected Compounds for a Heated Filament EI Source and VUV Krypton Lamp Source^a

	heated filament EI	VUV krypton lamp (10.6 eV)
toluene (IP 8.8 eV)	10	35
bromobenzene (IP 9.0 eV)	15	20
chloroform (IP 11.4 eV)	30	100

^a LODs are within 15% RSD. Ionization sources were gated/pulsed-on for only 20 ms per mass spectrum (see text for details).

Table 1 that the LODs are better for the heated filament source. In the case of chloroform, the IP lies well above the photon energy of the VUV krypton lamp and the LOD difference is larger. On the other hand, in the case of the samples that fall within the photoionization abilities of the VUV krypton lamp, the difference is smaller. In the latter case, the VUV krypton lamp may induce both photoionization and photoelectron impact ionization. In the former case, the mass spectra are most likely only due to photoelectron impact ionization. There are several factors that may contribute to the worse chloroform LODs for the lamp; for instance, the lamp brilliance is not very intense, not a lot of surface area inside the ion trap is illuminated, and the produced ions may not be in the best place for optimum trapping (which is in the middle of the trap) because the electrons will be accelerated between the illuminated area and the ring electrode. Thus, to

improve the LODs, another lamp with higher brilliance could be used and the geometry could be optimized such that a larger surface area inside the trap is illuminated. In any case, the comparable LODs are very promising.

CONCLUSIONS

An alternative ionization source for ion trap mass spectrometers based on a VUV lamp has been presented. This permits ionization to be performed by either photoionization or, as supported by the observed data, photoelectron impact ionization. In this manner, our observations suggest electron impact ionization can be used in ion trap mass spectrometers without the limitations of a heated filament. This can prove to be valuable in ion trap mass spectrometry applications where higher pressures are optimal or where portability requires low power consumption. Future work could include eliminating contributions from photoionization and measuring photoelectron energies to provide direct evidence of the photoelectron impact mechanism.

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