RESEARCH ARTICLE

Design Study of an Atmospheric Pressure Photoionization Interface for GC-MS

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GC-APPI-MS...

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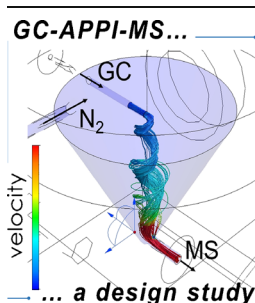
Abstract. This contribution reports on the development of an atmospheric pressure photoionization (APPI) source interfacing a gas chromatograph (GC) with a benchtop Orbitrap high resolution mass spectrometer (MS). We present efforts on method development aiming at high temperature stability (325°C), constant low impurity levels upon prolonged source operation, and efficient reaction volume irradiation combined with minimum peak broadening. The performance throughout each iterative development step was carefully assessed. The final GC-APPI-MS setup demonstrated femtogram-on-column sensitivity and chromatographic peaks of Gaussian shape with base peak widths <2 s for even the highest boiling compounds present in different EPA standard mixtures.

Keywords: GC-MS, APPI, Ion source development

Introduction

The motivation for the present work was the development of an alternative design for a sensitive GC-APPI interface for high-resolution mass spectrometry, allowing for efficient direct photoionization of eluting compounds. The historical way to the combination of generating photo-ions of a GC eluent at atmospheric pressure and subsequent transfer into a MS is quite long. We start in 1956, when Lossing and Tanaka employed sealed rare gas discharge lamps to generate photo-ions in the low pressure regime of a mass spectrometer [1]. The most common gas fillings are argon and krypton, which generate spectral outputs at 104.8/106.7 nm (11.8/11.6 eV) and 116.5/123.6 nm (10.6/10.0 eV), respectively. Photon fluxes of up to 10^{14} photons·s^{-1} are reported [2]. Over the decades, this type of light source has appeared in several different research disciplines requiring VUV radiation, including photochemical studies [2] or gas chromatography (GC) applications, as part of a photoionization detector [3]. Concurrently, the vacuum designs of mass spectrometers were tailored to accept higher sampling pressures and, in 1973–74, Horning et al. paved the way for the era of atmospheric pressure ion generation and sampling with the introduction of a Nickel-63 and corona discharge-based atmospheric pressure ionization (API) source [4, 5]. From here

on we got the impression that the history of introducing photoionization in API-MS is sometimes confusingly stated. In our view, Revelskii et al. introduced and patented the first combination of an API-MS interface with a VUV radiation source [6]. Samples were provided with either a GC [7] or a liquid chromatographic (LC) [8] stage. At that time, these authors coined the term "atmospheric pressure photoionization" (abbreviated as APPhI or APPI) [9]. Not much attention was paid to this new ionization method until 2000, when Syage et al. [10] and Robb et al. [11] reintroduced the combination of VUV radiating discharge lamps with LC-API sources. The foundation for commercialization was laid and LC-APPI-MS rapidly emerged as a standard analytical method [12].

The energy of the typically used VUV radiation, 10.0/10.6 eV, lies between the ionization energies (IEs) of common analyte molecules (IE < 10 eV) and LC-matrix components, such as air and most solvents (IE > 12 eV). Nevertheless, the majority of these matrix constituents, except nitrogen, exhibit strong absorption cross sections around 10 eV but do not ionize. The abundance of photo-physically and -chemically active compounds under LC conditions creates a black environment at the applied VUV wavelength for the relatively small amount of analyte [13] and, in addition, drives a rich neutral-radical photo-chemistry in which analyte ions potentially participate [14]. For these reasons, most LC applications showed poor direct photoionization efficiencies and low sensitivity

[15]. The APPI community swiftly addressed this sensitivity issue and introduced a photo-induced chemical ionization method, called "dopant assisted"-APPI (DA-APPI) [11]. Of note, Revelskii et al. introduced the exact same technique as atmospheric pressure photochemical ionization (APPhCI) 10 years before [16].

In contrast to LC, GC as an upstream separation method opens up completely different opportunities for the design and operation of an atmospheric pressure VUV ion source. When column bleeding and co-elution are negligible, GC provides well-separated compound packets in a chemically and photophysically inert matrix, which represents almost ideal conditions for APPI. Despite these benefits, the general field of GC-API did not gain much attention until 2005, when McEwen and McKay introduced a dual source LC/GC-APCI design compatible with Waters instrumentation [17]. Two years later followed the extension with a photoionization lamp [18]. In 2008, Luosujärvi et al. published a microchip-based GC-APPI approach [12, 19] and in the same year Bruker made a GC-API interface available for their instrumentation [20, 21]. In 2010, Waters followed with a GC-APCI ion source [22].

As stated, the motivation for the present work was the development of an alternative design for a sensitive GC-APPI interface, allowing for efficient *direct* photoionization of eluting compounds. Three key aspects were pursued: (1) simplicity of the matrix, (2) reasonable ionization efficiency, and (3) negligible impact on the chromatography. As described above, GC is advantageous over LC because of a much simpler matrix composition, and the same argument applies to the selection of the ionization method as well. Direct photoionization is a straightforward approach in terms of converting the supplied energy into the ionization process of the analyte, whereas any chemical ionization method requires several conversion steps with different species other than the analyte. This potentially complicates the acquired mass spectra and affects the stability of the source performance. In a theoretical section, we will first point out the relevant design aspects for a GC-APPI source design and subsequently move on to a practical implementation of a GC-APPI interface for a high-resolution bench-top Orbitrap mass spectrometer.

Experimental

Mass Spectrometer

The GC-APPI interface development focused on coupling the source assembly to the standard API inlet system of ThermoFisher Scientific (TFS, Bremen, Germany) Orbitrap mass spectrometers. For evaluation of the ion source performance, an Exactive Orbitrap MS, and additionally a modified Exactive MS with a compact, high-field Orbitrap analyzer (research-only), were employed [23]. The standard IonMax API housing and the ion sweep cone were removed and the electronic interlock was bridged with appropriate resistors to mimic an APPI/APCI operating mode. The original transfer capillary was replaced by a stainless steel capillary (0.5 mm inner diameter; Klaus Ziemer GmbH, Langerwehe, Germany), which was modified with a gas-tight adaptor connecting to the source assemblies. Particular care was taken when tuning the ion optics of the instrument. For this purpose, toluene vapor was added to the make-up gas and automatic tuning on m/z 92 was performed. In order to minimize the m/z 91/92 ratio (i.e., minimizing collisionally-induced fragmentation within the inlet region), the voltages in the first differential pumping stage were manually adjusted. The relative intensity of the dehydrogenated cation of toluene is used as a measure for harsh and unintended CID conditions, which arise from excessively strong potential gradients within the lower mbar pressure range. This tuning procedure aims for simultaneously efficient and soft ion transport conditions to enhance the overall chromatographic sensitivity. The standard Exactive MS provides four different mass resolving power settings from 10,000 to 100,000 with intrinsically changing scan rates from 10 to 1 Hz, respectively. This means that the instrument mapped the chromatographic elution profile with sufficient data points only at its lowest mass resolution. The modified research-only instrument, however, operated at a mass resolving power of 30,000 with a scan rate of 9 Hz.

Gas Chromatograph

A TRACE 1310 GC oven equipped with a TR-Dioxin 5MS column (30 m × 0.25 mm i.d. × 0.1 μm), both from TFS, was employed for chromatographic separation. A heated transfer line (TFS) was used to transfer the GC effluent from the oven to the APPI interface.

Light Source

A commercially available, low-pressure Kr discharge lamp with a 13.56 MHz electronic driver from Syagen (Santa Ana, CA, USA) provided VUV radiation at 10.0 and 10.6 eV. The rf driver is compatible with the MS instrument's electronics and software. It is noteworthy that in all the designed GC-APPI interface versions, the driver unit was exposed to extreme heat because of its spatial vicinity to the hot surfaces of the ion source assembly (cf. Figure 3). Nevertheless, during the entire development period, the lamp emission did not suffer from any noticeable intensity loss or variation. In an experimental study, which spanned 2 mo of extensive use, the integrated emission output between 200 and 1000 nm was monitored with a UV/VIS fiber optical spectrometer (AvaSpec-3648; Avantes BV, Apeldoorn, The Netherlands) at different ambient conditions. The measured intensity variation was below 10% and should correlate well with the VUV emission intensity, provided that the VUV light transmission properties of the MgF_2 window of the lamp remained constant as well. The stability of the VUV radiation output is the prerequisite for the analytical reproducibility. The experiments were carried out with the necessary precautions with respect to hazardous radiation as well as exposure to hot surfaces.

Theory on Ion Generation

The following model and assumptions are used to roughly estimate an upper limit of the generated ion concentration of an eluting compound in an exemplary ion source volume: a compound exits the GC column into the ion source as a "packet," thus maintaining its local concentration. The make-up gas determines the velocity of the traversing packet through the ionization region and hence determines its irradiation time. Any mixing with the make-up gas during the residence time in the irradiated volume is neglected. In addition, any heterogeneous gas velocity distribution within the ion source is also not taken into consideration.

We begin by estimating the mean analyte concentration at the exit of the GC column. If we consider a 2 pg on column injection of naphthalene with a molar mass of 128 g/mol, a total number of $9.4 \cdot 10^9$ molecules will elute during the chromatographic peak. Discarding peak broadening due to the ion source volume and assuming a chromatographic peak significantly simplified as being rectangular in shape with a 4 s base width, we obtain an elution velocity of approximately $2.4 \cdot 10^9$ molecule$\cdot$s^{-1} for this compound. With a typical column flow of 1.5 ml$\cdot$min^{-1} or 0.025 cm$^3 \cdot$s^{-1}, an approximate mean concentration, $c_{neutral}$, of $9.4 \cdot 10^{10}$ molecule$\cdot$cm^{-3} is derived. The residence time, t, which is identical to the irradiation time of a molecule in the ionization region, is 8.5 ms, which is calculated by dividing the source volume of 0.12 cm^3 (used in the present work) by the transfer capillary volume flow of 14.2 cm$^3 \cdot$s^{-1} (measured volume flow under typical operating conditions of the used instrumentational setup). Owing to the short residence time, we assume that the initial neutral analyte concentration exceeds the generated ion concentration by at least three orders of magnitude after "completion" of the ionization process. Hence, the photoionization rate will be pseudo-zero order with respect to the neutral analyte concentration. We thus obtain the following linear equation for the mean ion concentration, c_{ion}, generated during elution:

$$c_{ion} = c_{neutral} \cdot \Phi \cdot \sigma \cdot \varphi \cdot t \qquad (1)$$

where Φ is the photon flux of the VUV lamp (typically 10^{14} photons$\cdot$s$^{-1} \cdot$cm^{-2}), σ is the absorption cross section (in this wavelength range, σ is typically on the order of 10^{-17} cm$^2 \cdot$molecule^{-1}), and φ is the ionization quantum yield (assumed to be 1 molecule$\cdot$photon^{-1}). This yields a final mean ion concentration in the GC effluent of $8 \cdot 10^5$ ions$\cdot$cm^{-3}. Multiplication by the column flow of $2.5 \cdot 10^{-2}$ cm$^3 \cdot$s^{-1} leads to an ion current of $2 \cdot 10^4$ ions$\cdot$s^{-1}, which enters the mass spectrometer. Integration over the 4 s rectangular peak width results in $8 \cdot 10^4$ naphthalene ions, which should roughly correspond to the integrated area of the chromatographic peak (disregarding ion transfer losses).

Equation 1 suggests two important parameters for efficient ionization on which the design of a GC-APPI interface would significantly impact: (1) the spatial overlap of the neutral sample concentration, $c_{neutral}$, with the photon flux, Φ, and (2) the residence time, t, of the neutral sample in the irradiated volume.

First, keeping in mind that the compound packet eluting from the GC column represents the highest neutral sample concentration in the entire setup, the first parameter implies that, after elution, the compound packet has to be kept tightly intact and as close to the VUV lamp as possible. Second, the residence time in the irradiated volume should be as long as possible without compromising the GC separation performance.

To optimize the spatial radiation overlap with the GC-effluent volume, the emission distribution across the diameter of the VUV lamp exit window was determined experimentally. For this purpose, the lamp was mounted on a translational stage and moved laterally in 0.25 mm steps along the entrance aperture of a modified ARC VM-502 VUV spectrometer (Acton Research Corporation, Acton, MA, USA) [24, 25]. At each position, a wavelength scan between 110 and 140 nm was recorded, and the total integrated emission of each spectrum (summed peak area of the 10.0 and 10.6 eV emissions) was plotted as a function of the lamp position.

As depicted in Figure 1, the radiation distribution is centered around the main axis of the lamp with a radius of about 4 mm and corresponds roughly to a normal intensity distribution. This result means that the optimum light entrance aperture for a GC-APPI source should be within 8 mm in diameter; at least it should not exceed this dimension to avoid unnecessary source volume.

Results and Discussion

The GC-APPI development phase consisted of four iterations, in the following denoted as #I – #IV. Table 1 lists essential parameters and characteristics for each development step. Figure 2 shows a cut through the central ionization region of each of the first three versions and Figure 3 shows a drawing of source assembly #IV with a close-up of its ionization volume.
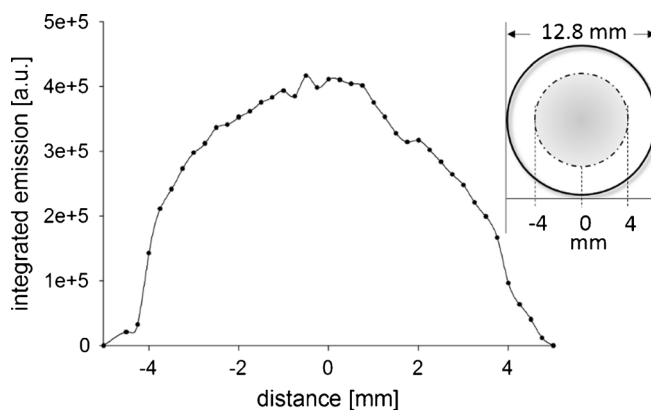
Figure 1. **Left panel:** Measured beam-profile of the total VUV radiation (10.0 and 10.6 eV) emitted by the discharge lamp [24]. Each data point represents the integrated light output of a 0.25-mm wide area along the complete cross section of the window at that point, as determined by the VUV-spectrometer. The experimental error is estimated to be within 5%. **Right panel:** Sketch of the lamp window marked with the net emitting area as measured

Table 1. Characteristic Properties of Each Source Developed in This Work

source version	I	II	III	IV
source body material	aluminium	aluminium	aluminium	Invar36
ionization volume [mm^3]	5	60	100	120
make-up gas [mL/min]	600	600	600 (split flow)	600–850
irradiation time [ms]	0.5	6	10–20	12
additional MgF$_2$ window	yes	no	no	yes
sealing material	Viton	Viton	FFKM	MgF$_2$ window cemented and coated with mineral sealing; graphite flat gaskets
surface finishing	no	no	no	polish and electrochemical gold coating
LOD of naphthalene [pg on column][a]	1 ng on column not detected	1	0.1	0.01[b]
peak-width (base) [s]	6	3	3	<2
peak - shape	Gaussian	Gaussian	Gaussian	Gaussian
linear dynamic range	not measured	5–500 pg	0.16–500 pg	0.01–1000 pg
		R = 0.995	R = 0.998	R = 0.998

[a]Extrapolated to the mass spectrometric signal-to-noise ratio of S/N = 3 based on the lowest concentrated injection. The noise level was determined by Qual Browser software
[b]The instrument setup was a modified Exactive MS with a compact, high-field Orbitrap analyzer and a S-lens interface [26]
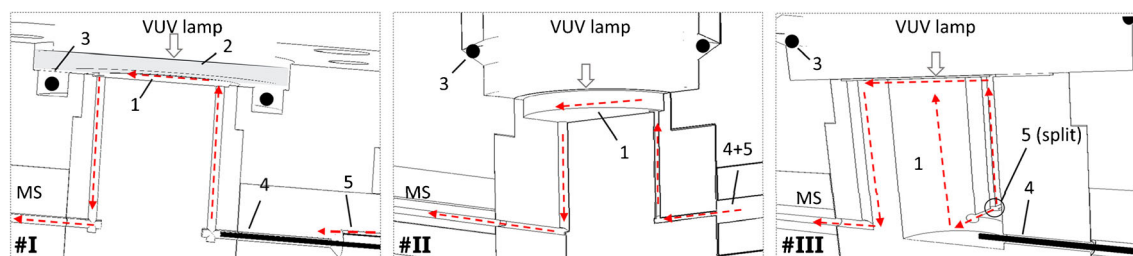
Iteration #I

Initial experiments were conducted using a comparably small cylindrical ionization volume of 5 mm^3, an irradiated area of 50 mm^2, and a height of 0.1 mm (cf. Figure 2, #I). The GC column and the sheathing make-up gas (N$_2$ with 99.999% purity; Messer Industriegase GmbH, Bad Soden, Germany) were guided directly into the heated source body. The make-up gas was adjusted with a 1 slm MKS mass flow controller and multigas controller 647C from MKS Instruments Deutschland (München, Germany). The diameter of all gas-flow channels was 0.5 mm, matching the diameter of the transfer capillary in the MS, A MgF$_2$ window with 1.5 mm thickness (Korth, Altenholz, Germany) and a standard Viton O-ring sealed the ionization volume. Although LiF has a higher transparency in the VUV region around 10 eV, MgF$_2$ is far less prone to heat stress and radiation-induced color centers (solarisation). The window of the VUV lamp was seamlessly surface-mounted to the MgF$_2$ window. The apertures of the source enclosure (transfer capillary entry, make-up gas/column connector) were O-ring sealed. Instead of a straight flow direction, technical design restrictions required an inverse U-type of flow with four sharp turning points (cf. Figure 2, #I). This seems to be against common sense concerning dead volumes and particularly ion wall losses. However, injections of headspace acetone revealed Gaussian shapes of the chromatographic peaks with ≤6 s base peak widths. The design of version #I,

however, did not show the targeted femtogram level sensitivity; a 1 μL injection of 1 ng/μL naphthalene in hexane was below the LOD.

Iteration #II

The poor sensitivity performance of #I was primarily attributed to the small irradiation volume. Accordingly, this volume was increased in version #II by an order of magnitude. Furthermore, the additional MgF$_2$ window was removed, which in principal reduces the VUV transmission by up to 10%. Instead, the window of the VUV lamp was directly attached to the surface of the ionization volume and O-ring sealed to the source enclosure (cf. Figure 2, #II). To minimize the transfer time to the ionization region, the GC effluent and the 600 mL/min make-up gas were premixed upstream in a make-up adapter (Valco fused silica make-up adapter 724FSMUAS15L; Machery-Nagel, Koblenz-May, Germany) and were flowed through the 0.5 mm channel making several turns before entering the transfer capillary. The N$_2$ make-up gas from compressed gas cylinders was further purified with a Vici Metronics (Poulsbo, WA, USA) N$_2$ purifier to sub-ppbv levels of impurities as stated by the manufacturer. The complex geometry of the source was again imposed by the required arrangement of the GC, the MS, and the make-up gas adapter. Nonetheless, this setup retained the Gaussian GC peak shape, and the base peak width was decreased by a factor of two to

Figure 2. From left to right, the first three iteration steps of the GC-APPI interface development: 1. Ionization volume, 2. MgF$_2$ window, 3. O-ring, 4. GC-column, and 5. make-up gas
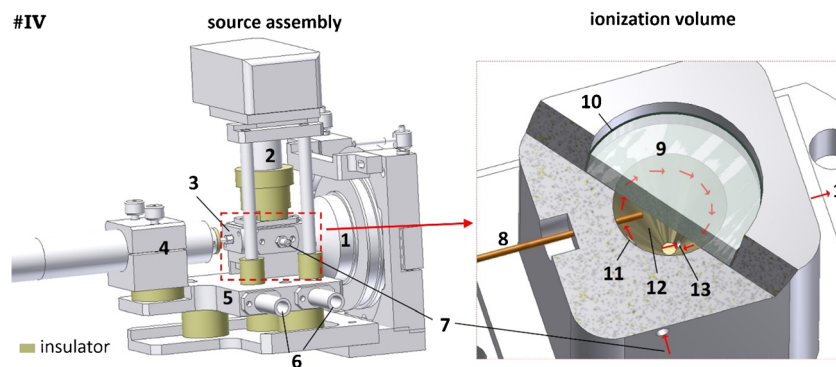
Figure 3. GC-APPI source interface #IV: 1. MS, 2. VUV lamp, 3. GC column adapter, 4. GC transfer line assembly, 5. heater table, 6. heater cartridges, 7. make-up gas adapter, 8. GC column, 9. MgF$_2$ window, 10. sealing with cement and inorganic coating, 11. make-up gas inlet, 12. conical ionization volume, 13. exit to MS

≤3 s, as measured with 100 pg naphthalene on column. With version #II, the LOD for naphthalene was approximately 1 pg on column, based on the extrapolated mass spectrometric signal-to-noise ratio, with the noise taken as calculated by the Xcalibur Qual Browser 2.2 software (TFS). The linear range was measured for naphthalene over two orders of magnitude from 5 to 500 pg on column with a regression coefficient of R = 0.995. The major drawback of version #II was the relatively high background of chemical noise and limited source temperature of ≤150°C, both caused by the use of standard Viton O-rings as sealing material.

Iteration #III

Four major changes were made when designing version #III (cf. Figure 2, #III): (1) implementation of high-temperature O-ring seals, (2) placement of the GC column exit port into the ionization volume, (3) splitting of the make-up gas flow, and (4) a further increase of the ionization volume. The newly implemented FFKM O-rings (V075B; Westring Dichtungstechnik GmbH, Köln, Germany) allowed source temperatures of up to 325°C and showed good form stability throughout a long-term test at maximum temperature. Nevertheless, the seal closest to the ionization volume around the glass body of the VUV lamp (cf. Figure 2, #III) led to permanent mass spectrometric interferences due to outgassing. This contamination effect appeared at source temperatures exceeding ~250°C and dominated the mass spectrum throughout the entire chromatographic run with a group of signals centered at *m/z* ~366. The second change enhanced the overlap of the analyte concentration and the photon flux. Direct infusion of the effluent into the irradiated volume replaced the premixing step of make-up gas and GC effluent from version #I and #II. Similarly, the introduction of a make-up gas split was intended to reduce the flow rate in the ionization region, thus leading to higher sample concentrations and longer residence times in the irradiated volume. Roughly two-thirds of the total make-up gas was introduced at the bottom of the ionization volume to support the transport of the GC effluent toward the VUV lamp, and one-third was guided toward the VUV lamp in a separate channel (cf. Figure 2, #III). The combined

gas streams left the source via a capillary channel with two U-turns before entering the transfer capillary. The analytical performance of version #III was investigated at 250°C source temperature to keep the background noise at an acceptable level. The chromatographic fidelity from version #II was retained, again with Gaussian GC peak shapes of base width of ≤3 s at 100 pg naphthalene on column. The linear range was measured from 160 fg to 500 pg naphthalene on column with a regression coefficient of R = 0.998 and an LOD of 100 fg.

Iteration #IV

A new fluid dynamic concept was introduced in the final version, #IV. The ionization volume is conically shaped with the exit port to the transfer capillary located at the apex, parallel to the GC column entrance port (cf. Figure 3; indices 13 and 8, respectively). Matching the spatial emission profile of the VUV lamp (cf. Figure 1), the circular cone base diameter is 8 mm; the lateral height of the cone is 7 mm, which results in an ionization volume of 120 mm^3 (cf. Figure 3; index 12). The GC column and the N$_2$ make-up gas entrance ports are located directly below the window; the latter is asymmetrically positioned to the far left of the cone and perpendicular to the GC column, as shown in Figure 3, indices 3 and 7, respectively. The GC entrance port is 0.4 mm closer to the window than the make-up gas entrance. Computational fluid dynamic (CFD) simulations, as shown in Figure 4a, support that in this configuration the main gas flow creates a sustained vortex inside the irradiated volume. The simulated massless particle traces of the GC flow in Figure 4b visualize the vortex drag exerted on the GC eluent, which results in a helical motion towards the apex. From a fluid-dynamic perspective, version #IV addresses the main issues concerning preservation of chromatographic fidelity and the key factors in Equation 1. As already discussed, Equation 1 states that with longer time, *t,* a more concentrated neutral analyte population, $c_{neutral,}$ will reside in a more densely irradiated volume, represented by Φ, and more analyte ions will be generated. For this reason, the eluent exit port in version #IV is positioned as close as possible to the divergent radiation source. Second, the rotational symmetry of the velocity distribution along the z-axis balances the temporal overlap of the GC
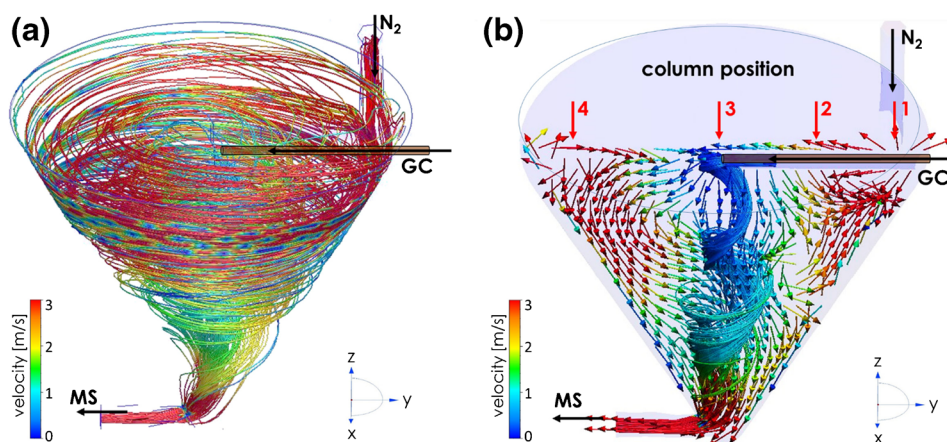
Figure 4. **(a)** Massless particle trace simulation of the make-up gas inside the conical ionization volume of version #IV. **(b)** Massless particle trace simulation of the GC eluent inside the conical ionization volume of version #IV. Additionally, the simulated velocity vectors in the y,z-plane are shown

peak and the irradiation time. While the temporal overlap of neutral analyte density and the photon flux is maximized with small velocity vectors in the x,y-plane as well as in z-direction, the irradiation time is increased with a larger x,y-velocity contribution, as it supports a circular movement with increasing radius. Furthermore, the simulated y,z-velocity vectors in Figure 4b reveal virtual absence of backward directed flow contributions. This translates to a zero dead volume configuration, and preservation of the primary peak shape as provided by the chromatography. This is confirmed by experimentally determined peaks of Gaussian shape and base width < 2 s (c.f. Table 1).

Experiments at different GC column positions gave some insight into the impact of the flow profile on the detected ion population. Figure 4b depicts four different column positions at which 10 pg naphthalene on column were injected, with three replicates at each position. At position 3, the analyte elutes exactly at the center axis of the vortex with a y-velocity magnitude of 0.5 m/s. In theory, this should be the optimum for the temporal overlap. However, in the experiments at this position, only 20% of the maximum attainable mass spectrometric response is reached. This is readily explained by the comparably small irradiation times. As illustrated in Figure 4b, virtually all velocity vectors in the center of the y,z-plane are small in magnitude; however, they also point directly to the apex, with only very low momentum in the x,y-direction. Positions 1 and 4 represent the other extreme with the analyte eluting close to the boundary of the vortex into a factor of six faster angular make-up gas velocity. This results in extended circular motion in x,y-direction with correspondingly increased irradiation times at the cost, however, of increased eluent dilution and possibly higher ion wall losses. Positions 1 and 4 gave similar results with roughly 80% of the maximum attainable intensity. These results strongly support the simulated rotational symmetry of the gas flow within the source. Maximum intensity was obtained in position 2, with the column located 2 mm off the center axis, reflecting an optimum balance between eluent confinement and irradiation time.

From a technical point of view, version #IV is the most advanced. As seen from the results obtained with version #III, even the highest temperature-resistant O-rings were not appropriate for the desired source cleanliness. Alternatively, the optical mount in #IV was attached with inorganic materials. First attempts to cement the VUV-lamp body directly into the source enclosure, however, failed due to mechanical strength. Thus, the concept of an additional window, at the cost of roughly 10% radiative loss, was re-invoked, with the benefit of much simpler and more rugged assembly. A MgF$_2$ window of 12.7 mm in diameter and 1.5 mm thickness was cemented (Omega CC High Temperature Cement; OMEGA Engineering, Inc., Stamford, CT, USA) into a 13-mm wide and 2-mm deep recess of the source enclosure (cf. Figure 3; indices 9 and 10, respectively). The enclosure itself was made of invar36 to match the small thermal expansion coefficient of the cement and MgF$_2$. With a cone base of 8 mm, the window and the enclosure formed a relatively large, highly polished annular contact surface of roughly 2.5 mm in width. Experiments with several different cements revealed severe leakage for all cements at temperatures above ~180°C, presumably due to increasing porosity. Repeated application of additional thin layers of an inorganic chromium oxide coating (Ipseal Khaki; Indestructible Paint, Ltd., Birmingham, UK) on the cement substantially reduced the leakage issue (cf. Figure 3; index 10). All remaining joints, such as the MS capillary adapter, the make-up gas adapter, and the GC-column adapter were sealed with Sigraflex graphite flat gaskets (A.W. Schultze, Geesthacht, Germany). A standard GC graphite ferrule connector established a gas tight connection between the GC column and the column adapter.

In version #IV, particular attention was paid to the surface inside the ionization region, since plain invar36 tarnishes and corrodes at higher temperatures to a nearly black-stained surface. The cone was thoroughly polished and afterwards electrochemically gold-coated. Attempts with gold sputtering failed primarily because of the cone apex region's poor

accessibility, which resulted in inhomogeneous gold layers. Furthermore, the sputtered gold did not prevent the ionization region from turning black after heating the invar36 material to 300°C. The electrochemical approach with a gold electrolyte solution from Conrad Electronic (Hirschau, Germany) generated a solid and smooth gold layer. While extensive use of the ion source (24/7 at 325°C for four months) did result in loss of brilliance, the gold layer prevented the cone from turning black and the surface remained smooth. The reflectance of electropolished gold coatings may reach 12% in the applied VUV range [27]; the efficiency of the electrochemical approach presented here is assumed to be below this value. It was speculated that a substantial increase of the surface reflectivity was attainable with an Al/MgF_2 double layer coating, which according to Hass and Tousey may reach up to 80% at 120 nm [28]. Unfortunately, an attempt with physical vapor deposition (PVD) of 200 nm and 25 nm thick layers of aluminum and MgF_2, respectively, did not lead to the expected reflectivity increase. Owing to the substantially higher effort and cost compared with the gold coating process, the PVD approach was not further pursued.

To avoid inhomogeneous electrical fields due to possible charging processes inside the capillary system, the path downstream of the ionization volume was made of a uniform 0.5 mm i.d. metal duct without any insulating material separating the MS metal capillary and the source enclosure. This design requires that the entire source block and heater table (cf. Figure 3; 5) floats on the MS transfer capillary voltage, an essential parameter for reasonable ion optics settings in the first differential pumping stage. Consequently, several electrical insulators were arranged around the ion source to maintain grounded mechanical mounts.

The analytical performance of version #IV was extensively evaluated using a modified Exactive MS with a compact, high-field Orbitrap analyzer [26]. A wide range of compounds, including compounds covered under several EPA methods (EPA 8081, EPA 527, EPA 8270, AOAC Method 2007.01), were analyzed. In total, 195 of 209 tested compounds, including but not limited to pesticides, FAMEs, phthalate esters, semi-volatiles compounds, aliphatic hydrocarbons, fragrances, and flame-retardants, were detected. The linear range for most compounds spanned five orders of magnitude from 10 fg to 1 ng on column with regression coefficients of R = 0.998 and inter-run reproducibilities of <30% RSD. Gaussian peak shapes with base widths of as low as 2 s were obtained. For more information on the analytical performance of the entire system the reader is directed to Peterson et al. [26], Kauppila et al. [29], Dousty [30], and Benter et al. [31].

Conclusions

From the presented work we conclude that a sustained vortex provides suitable flow conditions for the ionization volume of a GC-APPI-MS system. It allows the addition of a GC eluent to let it rotate through viscous forces in a plane perpendicular to the moving forward direction into the MS. In this way, intrinsically wide emission profiles of VUV-radiating lamps can efficiently be used with respect to eluent ionization, along with maintenance of the chromatographic fidelity.

Acknowledgments

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