

Spatially Confined Photoinduced Penning Ionization for Highly Sensitive Mass Spectrometry

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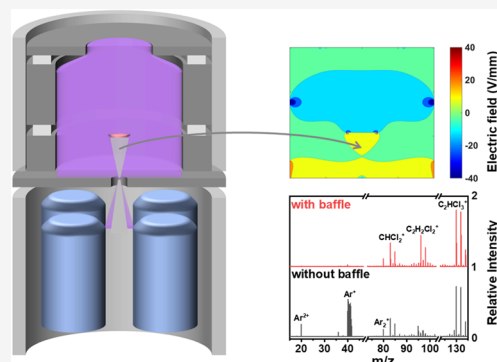


Article Recommendations



Supporting Information

ABSTRACT: In vacuum ultraviolet (VUV) lamp-based photoionization mass spectrometry (PI-MS), the axially mounted configuration exhibits higher sensitivity due to a longer light absorption path. However, VUV light irradiation of the metal surfaces within the transmission chamber induces photoelectron emission; excessive background gas ions are generated via photoelectron ionization under the radio frequency (RF) electric field, which affects the quantitative performance and repeatability of PI-MS, especially for deuterium lamps with a higher photon flux. In this study, a size- and position-adjustable baffle electrode was integrated into the ionization chamber to reduce the light leakage into the transmission chamber. For a 3 mm-diameter baffle positioned 5.4 mm from the skimmer, the intensity of background gas ions generated in the transmission chamber decreased to 1/506, while the intensity of the trichloroethylene ion was maintained at half that without the baffle. The intensities of chlorinated hydrocarbon ions were enhanced by 9-fold compared with the SPI mode when an RF voltage was further applied to the baffle electrode, under which the dominant ionization process was Penning ionization (PenI). Surprisingly, the intensities of chlorinated hydrocarbon ions did not decrease but increased by up to 126% compared to those without the baffle. Simulation of the electric field distribution and electron kinetic energy highlights that the precise overlap of the ion generation region and efficient transmission region plays a pivotal role in the regulation of spatially confined PenI toward sensitivity improvement. This approach has achieved limits of detection down to sub-pptv, even for molecules with ionization energies higher than the photon energy.



INTRODUCTION

Photoionization mass spectrometry (PI-MS) stands out as a robust analytical technique, primarily owing to its capacity for soft ionization of organic compounds.^{1–6} According to the Beer–Lambert law, the sensitivity of PI is positively correlated with light intensity and molecular number density.⁷ Because of the direct proportionality between molecular number density and pressure, sensitivity can be effectively improved from ppmv to pptv by increasing the pressure in the ionization chamber from below 1 Pa to kPa. However, as the pressure in the ionization chamber increases, the considerable pressure difference between the ionization chamber and the transmission chamber inevitably induces rapid ion expansion, resulting in substantial spatial and energy spread. Therefore, a radio frequency (RF) ion guide, such as a quadrupole, is required to enhance ion transmission efficiency.^{8–11}

Since the photon energy of vacuum ultraviolet (VUV) light is much higher than the work function of metals such as stainless steel, gold, and copper, photoelectrons are readily emitted when VUV light irradiates the metal electrodes in either the ionization chamber or the transmission chamber (via the ion extraction orifice). Excessive background gas ions are thus generated in the transmission chamber (10^0 Pa to 10^1 Pa)

via photoelectron ionization (PEI) due to the excessively high kinetic energy imparted to photoelectrons by the RF electric field acceleration.^{12–14} This attenuates detector response and lowers analyte ion transmission efficiency owing to the strong space charge effect, thereby affecting the quantitative performance and repeatability of PI-MS.

The performance of PI sources is closely related to the light sources, among which commercial krypton (Kr) lamps^{2,3,6,15–19} and deuterium (D_2) lamps^{20–22} are commonly used. Both axial-mounted^{8,13,14,16,18,19} and side-mounted^{15,17,20,22–24} coupling modes are applicable to the lamp and ionization chamber. The axial-mounted VUV lamp provides a longer optical absorption path, which enables a higher sensitivity. The side-mounted configuration avoids direct irradiation on the ion extraction orifice of the ionization chamber, thereby reducing VUV light leakage into the

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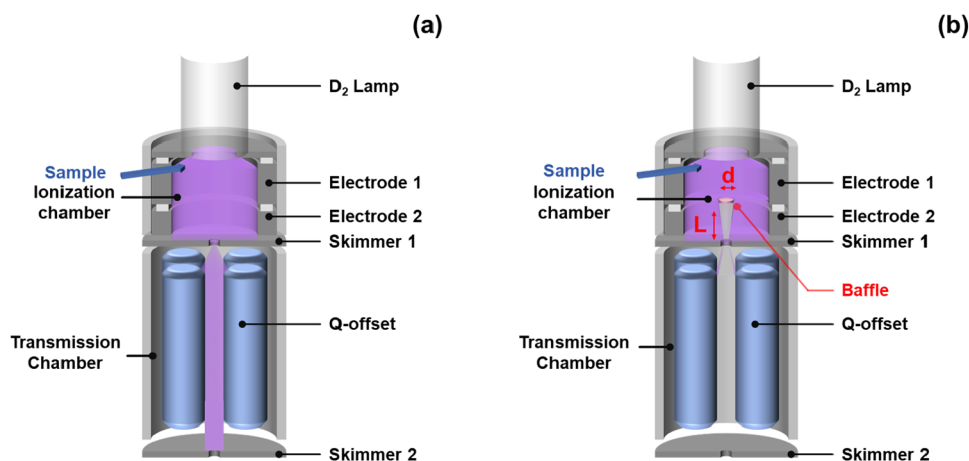


Figure 1. Schematic diagrams of the ion source and ion transmission optics, along with the spatial distribution of the VUV beam: (a) without baffle; (b) with baffle.

Table 1. Analytical Performance (In Counts per Second per Parts per Billion, cps/ppbv; 1 ppbv = 10^{-9} v/v; 1 pptv = 10^{-12} v/v) of Three Chlorinated Hydrocarbons; Comparison of the Sensitivity and LOD of CHCl_3 between This Study and Previous Literature

	compounds	chemical formula	IE (eV)	characteristic peak	sensitivity (cps/ppbv)	LOD (pptv)	linear range (pptv)	R^2
this work IFPI ¹⁹ EUV-PI ²⁶	trichloromethane	CHCl_3	11.37	CHCl_2^+	1025	0.197 (60 s)	2–5000	0.9989
					367	2.3 (10 s)		
					195	24 (30 s)		
this work	1,1,2-trichloroethane	$\text{C}_2\text{H}_3\text{Cl}_3$	11.48	$\text{C}_2\text{H}_2\text{Cl}_2^+$	1322	0.139	2–5000	0.9993
this work	trichloroethylene	C_2HCl_3	9.46	C_2HCl_3^+	4154	0.060	2–5000	0.9972

transmission chamber and the resulting background gas ions. In a side-mounted configuration, the D_2 lamp exhibits much higher light intensity than the Kr lamp, achieving a 17-fold increase in sensitivity, yet its absolute sensitivity remained relatively low.²² Therefore, higher sensitivity can be achieved using an axial-mounted D_2 lamp configuration, but the problem of excessive background gas ions needs to be addressed.

In this study, a baffle was employed to reduce light and background ion generation in the transmission chamber, with a high photon flux D_2 lamp axially mounted in the ionization chamber. To avoid the low light utilization efficiency and sensitivity loss caused by the baffle, an RF voltage was superimposed on the baffle to induce Penning ionization (PenI) or chemical ionization (CI). The size and position of the baffle and the RF voltage application mode were adjusted to improve sensitivity.

EXPERIMENTAL SECTION

Instrumentation

This study was conducted using the previously reported home-built time-of-flight mass spectrometer (TOFMS)²³ with notable improvements made to the ionization source. Figure 1a displays the schematic diagram of the ion source (without baffle) and ion transmission optics, along with the spatial distribution of the VUV beam. The ionization chamber was a cylindrical space with an inner diameter of 14 mm and a length of 15.1 mm, comprising a D_2 lamp (L7293, Hamamatsu Photonics K.K., Japan, 115–400 nm, photon energy up to 10.78 eV), Electrode 1, and Electrode 2. A skimmer electrode (Skimmer 1) with a 1 mm orifice served as the interface between the ionization chamber and the transmission chamber. The transmission chamber consisted of an RF-only quadrupole and another orifice electrode (Skimmer 2). All of the electrodes were made of stainless steel. Under VUV irradiation, photoelectrons could be generated from

the surface of Skimmer 1 within the ionization chamber. In addition, a portion of the light passed through the orifice of Skimmer 1 and irradiated the surfaces of the RF-only quadrupole and Skimmer 2, thereby leading to the photoelectron emission also within the transmission chamber.

As shown in Figure 1b, a 50 μm -thick round stainless steel baffle was mounted on and integrated with Electrode 2. The diameter of the baffle was defined as d , and its distance from Skimmer 1 as L . The VUV photons entering the transmission chamber could be effectively reduced by adjusting d and L . Pressures in the ionization chamber and the transmission chamber were maintained at 2400 and 10 Pa, respectively, as measured by two Pirani gauges (nAPG-LC RS485 NW16, Edwards Vacuum, West Sussex, U.K.). The acquisition time for all mass spectra in this work was set to 10 s (60 s for the sensitivity measurements in Table 1), with parallel experiments conducted at least three times.

Sample Selection and Preparation

Three chlorinated hydrocarbons relevant to the environment^{25–28} were selected as model molecules to characterize the performance of the ionization source. Among them, trichloroethylene (C_2HCl_3 , ionization energy (IE) = 9.46 eV) could be directly ionized via SPI, whereas trichloromethane (CHCl_3 , IE = 11.37 eV) and 1,1,2-trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$, IE = 11.48 eV) could not. A standard gas mixture containing 1 ppmv of each chlorinated hydrocarbon (C_2HCl_3 , CHCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) in argon (Ar, 99.999%) was supplied by Dalian Special Gases Co., Ltd. (Dalian, China). High-purity Ar (99.999%) was supplied by the Dalian Institute of Chemical Physics (Dalian, China). Gaseous samples were diluted to the target concentrations by employing a mass flow controller system (Beijing Sevenstar Electronics Co., Ltd., Beijing, China) before introduction into the ionization chamber.

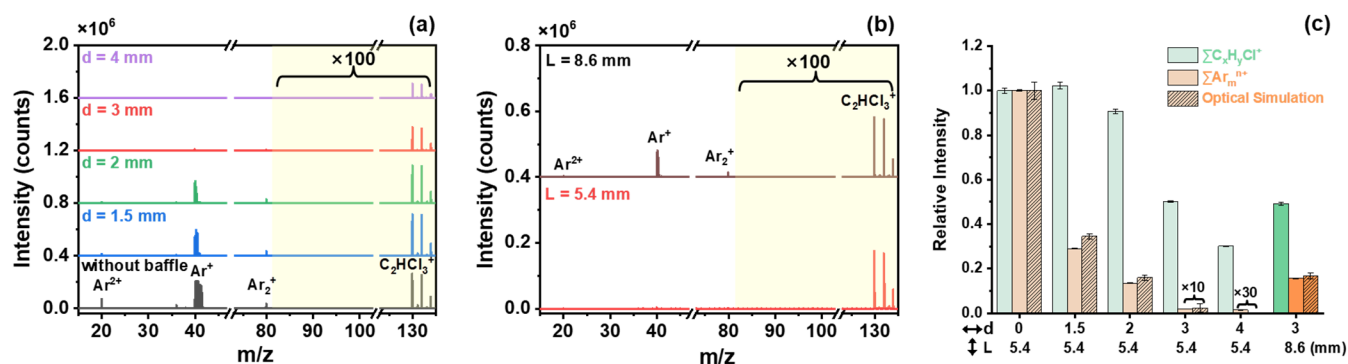


Figure 2. In SPI mode, (a) mass spectra of a standard gas mixture containing 2 ppbv of each chlorinated hydrocarbon (trichloromethane, 1,1,2-trichloroethane, and trichloroethylene) without baffle and with baffle diameters of 1.5, 2, 3, and 4 mm ($L = 5.4$ mm). (b) Mass spectra with a distance of 5.4 mm and 8.6 mm from the baffle to Skimmer 1 ($d = 3$ mm). (c) Relative intensities of total chlorinated hydrocarbon ions, total argon ions, and light intensity obtained through optical simulation, normalized to the values without baffle.

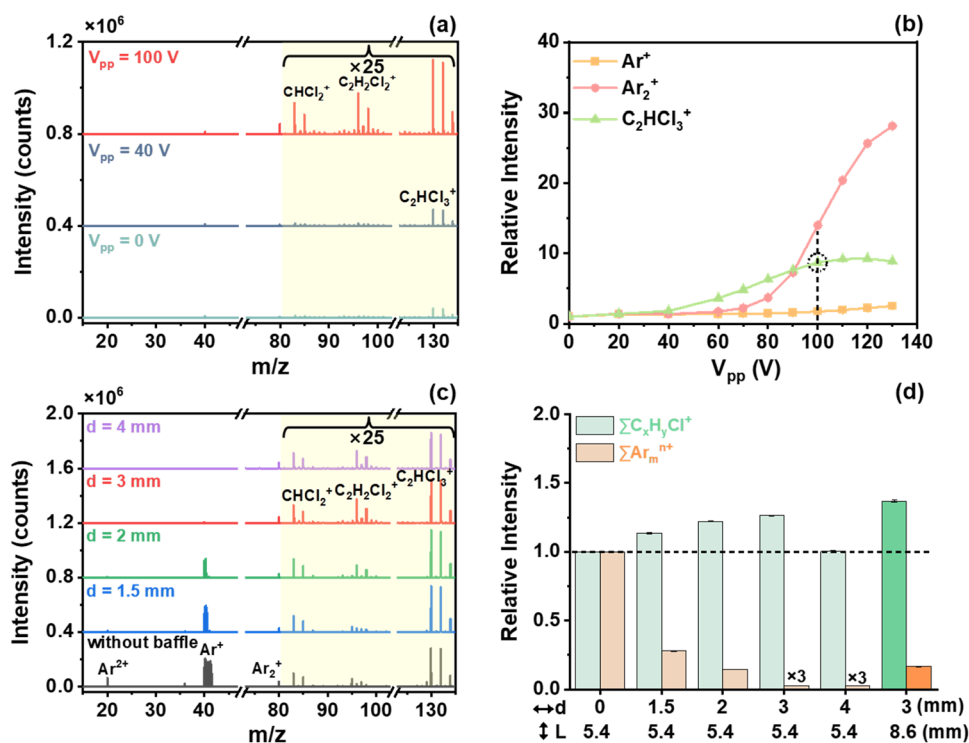


Figure 3. (a) Mass spectra with RF voltages applied to the baffle ($d = 3$ mm, $L = 5.4$ mm) at a frequency of 1 MHz and V_{pp} of 0 V (SPI), 40 V, and 100 V. (b) Relative intensities of Ar^+ , Ar_2^+ , and $C_2HCl_3^+$ as a function of V_{pp} normalized to the values in SPI mode ($d = 3$ mm, $L = 5.4$ mm). (c) Mass spectra without baffle and with baffle diameters of 1.5, 2, 3, and 4 mm ($L = 5.4$ mm) at $V_{pp} = 100$ V. (d) Relative intensities of total chlorinated hydrocarbon ions and total argon ions with different baffle diameters and positions normalized to the values without a baffle.

RESULTS AND DISCUSSION

Baffle Performance

In SPI mode, the voltages applied to Electrode 1, Electrode 2, and Skimmer 1 were 17, 16.5, and 14 V, respectively. This electric field configuration prevented the acceleration of photoelectrons generated in the ionization chamber, thereby avoiding the PEI process. Figure 2a shows the mass spectra of a gas mixture containing 2 ppbv of each chlorinated hydrocarbon (C_2HCl_3 , $CHCl_3$, and $C_2H_3Cl_3$) acquired under SPI mode without a baffle and with baffle diameters of 1.5, 2, 3, and 4 mm ($L = 5.4$ mm). Figure 2b presents the mass spectra obtained with distances of 5.4 mm and 8.6 mm ($d = 3$ mm) from the baffle to Skimmer 1. A light field model was established to simulate the light intensity passing through the

orifice on Skimmer 1 into the transmission chamber, under the assumption that the argon-ion intensity was proportional to the light intensity. Methods for simulating photon path tracing in the D_2 lamp-based ionization source are available in the Supporting Information. Normalized to the values without baffle, relative intensities of total chlorinated hydrocarbon ions (only $C_2HCl_3^+$), total argon ions (Ar^{2+} , Ar^+ , and Ar_2^+), and simulated light intensity are plotted in Figure 2c. The ion generation region was deduced from the differences in ion intensity observed in mass spectra acquired under different voltage modes, as shown in Figure S5. In mode (a), ions generated both in the ionization chamber and the transmission chamber were detected, while in mode (b), only ions generated in the transmission chamber were detected. These results indicate that chlorinated hydrocarbon ions were

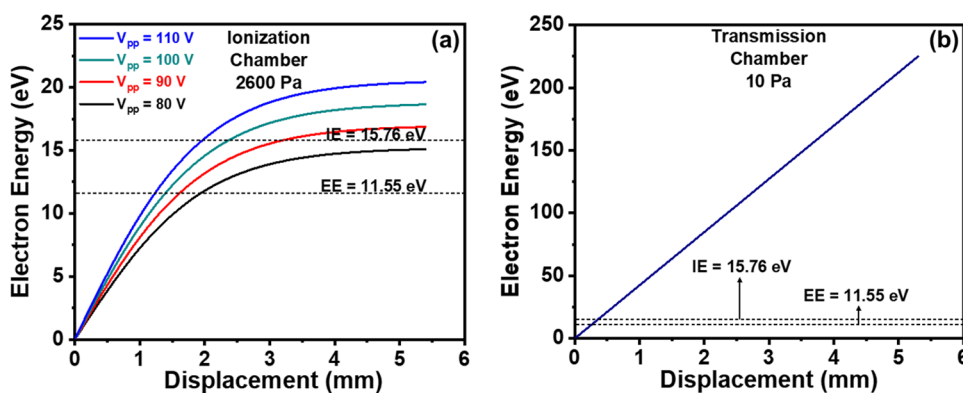


Figure 4. Electron kinetic energy as a function of displacement (a) with different V_{pp} applied to the baffle in the ionization chamber (2600 Pa) and (b) in the transmission chamber ($p = 10$ Pa).

generated in the ionization chamber via SPI, and argon ions were generated in the transmission chamber via PEI induced by the D_2 lamp light passing through Skimmer 1. Optical simulation and experimental ($\sum Ar_m^{n+}$) results showed good consistency.

After the baffle was mounted on Electrode 2, the argon-ion intensity significantly decreased with increasing baffle diameter. When the baffle diameter reached 3 mm, the relative intensity of argon ion decreased to only 1/506 of that without the baffle. Interestingly, although the baffle was positioned along the ion transmission path within the ionization chamber and its size exceeded the inner diameter of the ion exit orifice on Skimmer 1 (1.5–4 mm vs 1 mm), its impact on the $C_2HCl_3^+$ ion signal intensity was relatively minor. At a baffle diameter of 3 mm, the $C_2HCl_3^+$ ion signal intensity remained at 50% of the value without the baffle, and at 4 mm, it remained at 30%. This can be attributed to two main factors. First, SPI could still occur outside the baffle region to produce $C_2HCl_3^+$ since the diameter of the VUV light beam emitted from the D_2 lamp (8 mm) was larger than that of the baffle diameters (1.5–4 mm). Second, ions close to Skimmer 1 can pass through its orifice more easily under the drag force from the pressure difference between the ionization chamber and the transmission chamber. In particular, ions generated near the axis of the ionization chamber or in the vicinity of the Skimmer 1 orifice could be efficiently drawn into the transmission chamber.²⁹ Given the trade-off between reducing background argon ions and preserving analyte signal, a 3 mm diameter baffle was finally adopted. It is interesting to note that the distance from the baffle to Skimmer 1 appeared to have a negligible effect on the intensity of chlorinated hydrocarbon ions, but significantly affected the intensity of argon ions. As shown in Figure 2b and the dark columns in Figure 2c, the light-blocking ability of the baffle was about 79-fold stronger at the distance $L = 5.4$ mm from Skimmer 1 than at the distance $L = 8.6$ mm. Therefore, a 3 mm-diameter baffle positioned 5.4 mm from Skimmer 1 represented the optimal baffle configuration.

Figure 3a presents the mass spectra obtained with RF voltages superimposed on the baffle ($d = 3$ mm, $L = 5.4$ mm) at a frequency of 1 MHz and peak-to-peak amplitudes (V_{pp}) of 0 V (SPI), 40 V, and 100 V. Figure 3b shows relative intensities of Ar^+ , Ar_2^+ , and $C_2HCl_3^+$ as a function of V_{pp} , normalized to the values in SPI mode ($d = 3$ mm, $L = 5.4$ mm). The baffle performance with an RF voltage ($f = 1$ MHz, $V_{pp} = 100$ V) is shown in Figure 3c,d, and discussed in the “Spatially Confined Penning Ionization” section. With the

application of RF voltage, the relative intensity of $C_2HCl_3^+$ increased with V_{pp} and reached a plateau at about 100 V, achieving a 9-fold enhancement compared with SPI mode. Besides, ionization products of trichloromethane ($CHCl_2^+$) and 1,1,2-trichloroethane ($C_2H_2Cl_2^+$) appeared, which could not be ionized in SPI mode due to higher IEs (11.37 and 11.48 eV) than the photon energy (10.78 eV). Likewise, as shown in Figure S5, differences across voltage modes indicate that all chlorinated hydrocarbon ions were generated in the ionization chamber.

Such enhanced sensitivity of C_2HCl_3 and expanded range of ionizable species ($CHCl_3$ and $C_2H_3Cl_3$) were attributed to PenI involving Ar^* and/or CI involving Ar^+ (Ar_2^+), which were initiated by photoelectrons with certain kinetic energy obtained from the electric field.²⁴ The kinetic energy (ϵ) balance of the electron is given by eq 1, assuming an elastic collision between the electron and background gas.³⁰

$$\frac{d\epsilon}{dt} = (\Delta\epsilon_E - \delta\epsilon)\nu_m \quad (1)$$

where $\Delta\epsilon_E$ is the mean energy gained by an electron in one effective collision, δ is the background gas-dependent electron kinetic energy loss coefficient, and ν_m is the effective collision frequency for momentum transfer.

Electron kinetic energy as a function of displacement could be derived as

$$\epsilon = \frac{\alpha\gamma}{p} \frac{e^{(\beta p/\gamma)x} - 1}{e^{(\beta p/\gamma)x} + 1} \quad (2)$$

where $\alpha = \frac{\sqrt{3\pi}eE}{4\sqrt{\delta}}$, $\beta = \frac{8\sqrt{\delta}}{\sqrt{3\pi}}$, $\gamma = \frac{RT}{N_A\sigma_{tr}}$, e is the charge of the electron, E is the electric field strength, and σ_{tr} is the momentum transfer cross section. More detailed derivation processes were presented in previous work.²⁴

The electron energy as a function of displacement is plotted in Figure 4a for different V_{pp} values applied to the baffle in the ionization chamber, based on the electron kinetic energy equation (eq 2). For an applied V_{pp} of 80 V, the maximum electron energy (15.09 eV) exceeded the excitation energy (EE) of the Ar^* metastable state (3P_2 , 11.55 eV) but lay below the IE of Ar (15.76 eV). Consequently, only Ar^* was generated, leading to the occurrence of PenI. When a V_{pp} of 90 V was applied, a small fraction of electrons acquired energies exceeding the IE of Ar, leading to the generation of argon ions and the subsequent CI process of analyte molecules. Both PenI and CI contributed to the improved sensitivity for

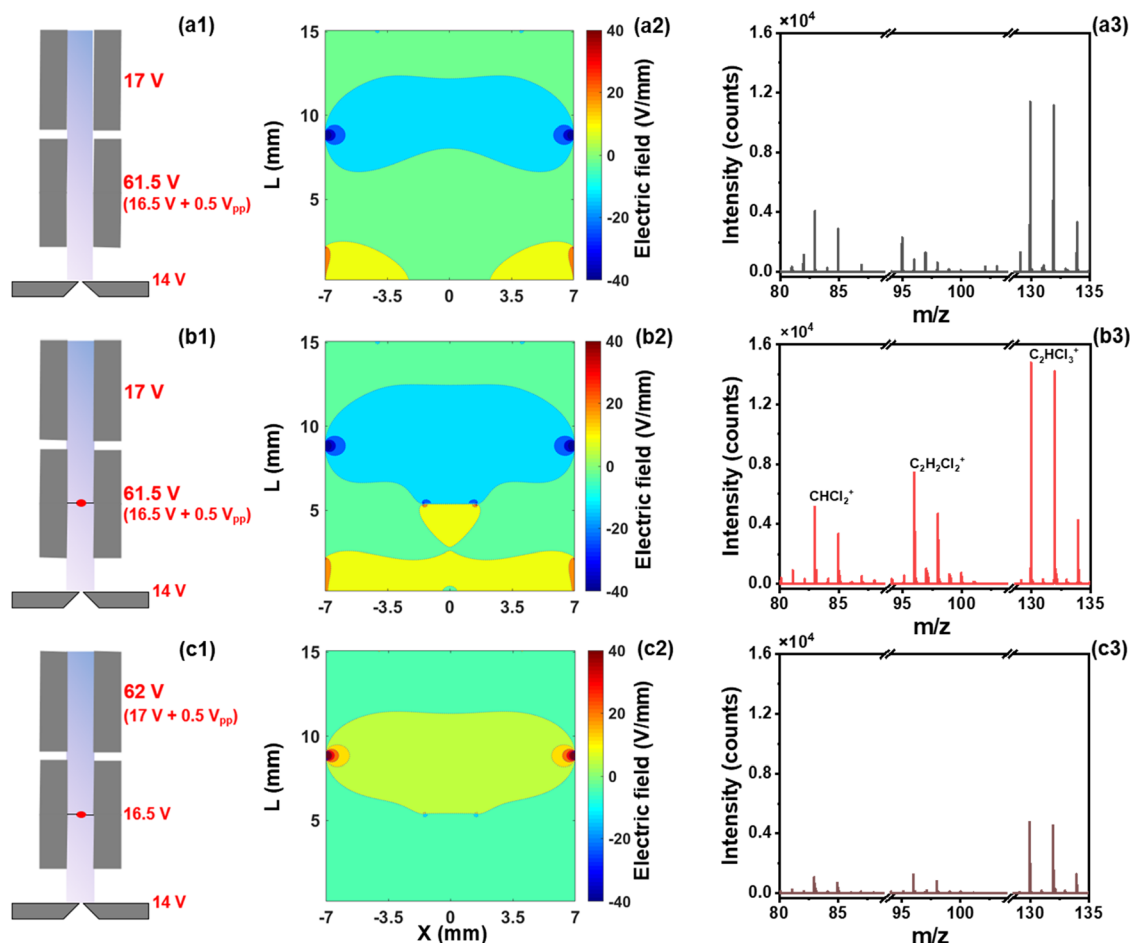


Figure 5. Schematic diagram of the RF voltage ($f = 1$ MHz, $V_{pp} = 90$ V) at crest applied to Electrode 2 without baffle (a1) and corresponding electric field strength distribution (a2) and mass spectrum (a3). Schematic diagram of the RF voltage applied to Electrode 2 with baffle (b1, $d = 3$ mm, $L = 5.4$ mm) and corresponding electric field strength distribution (b2) and mass spectrum (b3). Schematic diagram of the RF voltage applied to Electrode 1 with baffle (c1, $d = 3$ mm, $L = 5.4$ mm) and corresponding electric field strength distribution (c2) and mass spectrum (c3).

C_2HCl_3 and the ionization of chlorinated hydrocarbons with high IEs ($CHCl_3$ and $C_2H_3Cl_3$).

The argon ions in the transmission chamber were generated via the PEI. The electron energy as a function of displacement in the transmission chamber ($p = 10$ Pa) is plotted in Figure 4b. Owing to the relatively high electric field strength (V_{pp} of the RF voltage applied to the quadrupole was 450 V) and the low pressure in the transmission chamber, the kinetic energy of most electrons exceeded the IE of Ar. Hence, the PEI process dominated in the transmission chamber.

Since Ar^+CI might induce ion fragmentation and result in poor selectivity and complex mass spectra, the optimal V_{pp} should be set to the maximum value at which Ar^* metastable states were generated while argon ions were not, thus ensuring that the ionization mode was pure PenI. Argon ions might be generated in either the ionization chamber or transmission chamber, depending on V_{pp} . To identify the region of argon-ion generation, different voltage application modes were employed, analogous to those in SPI mode (Figure S5), and the results are shown in Figure S6. The optimal V_{pp} was determined by the pressure in the ionization chamber, exhibiting good agreement with the theoretical calculation results, as displayed in Figure 4a. Given that higher chlorinated hydrocarbon ion intensities and lower argon-ion intensities were achieved at 2600 Pa with 90 V_{pp} compared with 2400 Pa

with 80 V_{pp} , the 2600 Pa with 90 V_{pp} condition was adopted for subsequent experiments, where PenI was the dominant ionization process.

Spatially Confined Penning Ionization

The influence of baffle diameter and position was investigated under an applied voltage ($f = 1$ MHz, $V_{pp} = 100$ V), as illustrated in Figure 3c,d. The total argon-ion signal exhibited a trend similar to that in the SPI mode, indicating that the light-blocking effect of the baffle remained effective. It was surprising that the total chlorinated hydrocarbon ions ($C_2HCl_3^+$, $CHCl_2^+$, and $C_2H_2Cl_2^+$) even exhibited higher intensity at certain baffle diameters (1.5 mm, 2 mm, and 3 mm) than those without a baffle. The light intensity irradiated on Skimmer 1 was reduced by approximately 4%, 6%, and 14% with baffle diameters of 1.5, 2, and 3 mm, respectively (see the Supporting Information). Nevertheless, the ion intensities of chlorinated hydrocarbons increased by 14%, 22%, and 26% with an RF voltage superimposed on the baffle, respectively.

To elucidate this anomalous increase in chlorinated hydrocarbon ion intensity, simulations of the electric field strength distribution were performed using SIMION 8.1 (Figure S2a,b2). Compared with the baffle-free configuration (Figure S2a2), the presence of a baffle (Figure S2b2, $d = 3$ mm, $L = 5.4$ mm) produced a high electric strength field zone that was more centrally located and closer to Skimmer 1. This field

enhancement enabled photoelectrons to be accelerated more rapidly to the EE of Ar, thereby the chlorinated hydrocarbon ions generated by PenI of Ar* were closer to Skimmer 1 in Figure S**5b1** than those in Figure S**5a1**, resulting in higher ion transmission efficiency.²⁹

Different RF voltage application modes were also investigated under a fixed baffle configuration ($d = 3$ mm, $L = 5.4$ mm). When the RF voltage was applied to Electrode 1 (Figure S**5c1**), the high electric field strength zone (also the spatial region of PenI) concentrated above the baffle and was far from the axis of the ionization chamber (Figure S**5c2**), and the sensitivity (Figure S**5c3**) was approximately one-third of that when the RF voltage was applied to Electrode 2 (Figure S**5b3**). This indicated that ions above the baffle could hardly pass through Skimmer 1, and the region below the baffle near Skimmer 1 corresponded to the high ion transmission efficiency region. In other words, the sensitivity improvement in PenI might be attributed to the spatial confinement effect, i.e., the ion generation region and the efficient transmission region overlapped precisely under proper baffle and voltage conditions. The optimal baffle conditions were 3 mm in diameter and 5.4 mm from Skimmer 1, with an RF voltage applied to Electrode 2. The PenI zone was confined between the baffle and Skimmer 1, as shown in the yellow area in Figure S**5b2**.

Linear calibration curves for three chlorinated hydrocarbons are shown in Figure S**7**, and the analytical performance of the three chlorinated hydrocarbons is presented in Table 1. The 3σ limits of detection (LOD, 60 s signal integration) of trichloromethane, 1,1,2-trichloroethane, and trichloroethylene were 0.197, 0.139, and 0.060 pptv, respectively. Figure S**8** displays the mass spectrum of a standard gas mixture containing 2 pptv of each compound (trichloromethane, 1,1,2-trichloroethane, and trichloroethylene) with a baffle ($d = 3$ mm, $L = 5.4$ mm) in PenI mode (2600 Pa, $V_{pp} = 90$ V) and an acquisition time of 60 s. The sensitivity of CHCl_3 in this work was enhanced by 3-fold compared with our latest IFPI source¹⁹ while ensuring low fragmentation. Table 1 also provides further comparisons of sensitivity and LODs between this study and previous literature.

CONCLUSIONS

In this study, a size- and position-adjustable baffle electrode was integrated into an ionization chamber. Background gas ions generated in the transmission chamber had been effectively reduced, with little impact on the intensity of chlorinated hydrocarbon ions in the SPI mode. The intensity of C_2HCl_3^+ was enhanced by 9-fold compared with the SPI mode, and ionization products of trichloromethane (CHCl_2^+) and 1,1,2-trichloroethane ($\text{C}_2\text{H}_2\text{Cl}_2^+$) with higher IE than the photon energy appeared when an RF voltage was applied to the baffle, under which the dominant ionization process was PenI. Surprisingly, the intensities of chlorinated hydrocarbon ions did not decrease but increased by up to 126% compared with those without the baffle. As indicated by the electric field strength distribution, the sensitivity improvement of PenI might be attributed to the spatial confinement effect, that is, the ion generation region and the efficient transmission region overlapped precisely under proper baffle and voltage conditions. The spatially confined photoinduced PenI source designed in this study achieved high sensitivity (sub-pptv) while ensuring low fragmentation, which demonstrates broad

application prospects for the analysis of complex trace-level samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.6c01680>.

Simulation of photon path tracing in the D_2 lamp ionization model (Figures S1–S4 and Table S1); calculation of the light-blocking ratio; determination of the ion generation region (Figure S5); intensity of total chlorinated hydrocarbon ions, intensity of total argon ions generated in the ionization chamber, and percentage of argon ions generated in the ionization chamber as a function of V_{pp} at 2400 and 2600 Pa (Figure S6); linear calibration curves for three chlorinated hydrocarbons (Figure S7); mass spectrum of a standard gas mixture containing 2 pptv of each chlorinated hydrocarbon (Figure S8) (PDF)

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Author Contributions

This manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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