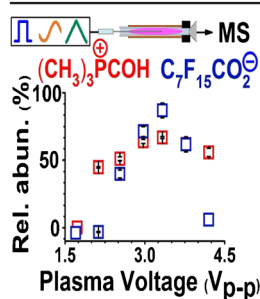


Effects of Different Waveforms on the Performance of Active Capillary Dielectric Barrier Discharge Ionization Mass Spectrometry

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Abstract. Active capillary dielectric barrier discharge ionization (DBDI) is emerging as a compact, low-cost, and robust method to form intact ions of small molecules for detection in near real time by portable mass spectrometers. Here, we demonstrate that by using a 10 kHz, ~2.5 kV_{p-p} high-voltage square-wave alternating current plasma, active capillary DBDI can consume less than 1 μW of power. In contrast, the power consumed using a sine and triangle alternating current waveform is more than two orders of magnitude higher than that for the square waveform to obtain a similar voltage for plasma generation. Moreover, the plasma obtained using a square waveform can be significantly more homogenous than that obtained using sine and triangle waveforms. Protonated dimethyl methylphosphonate (DMMP) and deprotonated perfluorooctanoic

acid (PFOA) can be detected at about the same or higher abundances using square-wave DBDI mass spectrometry compared with the use of sine and triangle waveforms. By use of benzylammonium thermometer ions, the extent of internal energy deposition using square, sine, or triangle waveform excited plasmas are essentially the same at the optimum voltages for ion detection. Using an H-bridge circuit driving a transformer optimized to reduce losses, square-wave active capillary DBDI can be continuously powered for ~50 h by common 9 V-battery (PP3).

Keywords: Dielectric barrier discharge ionization, Low temperature plasma ionization, Thermometer ions, Portable mass spectrometry, Dimethyl methyl phosphonate, Perfluorooctanoic acid, Chemical warfare agents, Nerve agents, Persistent organic pollutants

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Introduction

Ambient ionization methods are recognized for their ability to form intact analyte ions from their in situ environment for detection by mass spectrometry (MS) with high sensitivity in near real time [1–3]. Ions can be formed under ambient conditions using plasmas, sprays, laser desorption, and photoionization-based approaches [1–3]. Plasma ion sources have the advantages that (1) molecules of relatively low polarity can be efficiently ionized and detected, and (2) analytes, e.g., dimethyl methylphosphonate, can be detected directly from relatively complex samples with reduced matrix ion suppression effects [4, 5].

Dielectric barrier discharge ionization (DBDI) is an emerging method in which a high voltage alternating electric field is used

to initiate the electrical breakdown of a gas at ambient pressure to ionize neutral gas-phase analyte molecules by proton transfer reactions [4–7]. The plasma can generate intact organic ions with labile bonds that can be detected with minimal fragmentation [8]. For example, using 4-substituted benzyl ammonium thermometer ions, the extent of internal energy deposition by use of DBDI was significantly lower than that of atmospheric pressure chemical ionization under a wide range of conditions [8].

In ‘active capillary’ DBDI [9, 10], the plasma ionizes ambient air and volatile neutral analyte molecules as they flow into the capillary entrance of the mass spectrometer owing to suction from the vacuum interface (Figure 1). This active capillary design eliminates the use of compressed gases, which is beneficial for minimizing the size of the ion source for applications in portable ion detection. For example, active capillary DBDI-MS has been used to detect chemical warfare agent simulants in air at levels below 10 μg m⁻³ (<10 ppb) using a portable mass spectrometer [11]. For complex mixtures, the ion source can be directly interfaced with solid phase microextraction (SPME) to

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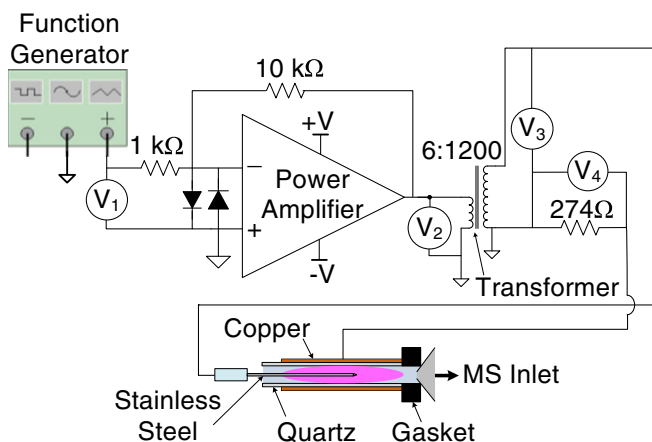


Figure 1. Circuit for forming a dielectric barrier discharge plasma using a square, sine, or triangular waveform. The input (V_1), output (V_2), and plasma (V_3) voltages, and plasma current (V_4/R) are indicated ($R = 274 \Omega$)

reduce ion suppression [12, 13]. Recently, we demonstrated that SPME-DBDI can be used to detect nerve agent simulants at low ppb levels directly from urine and seawater without sample preparation or chromatography in measurements that take less than 2 min [12].

A key design consideration of dielectric barrier discharge ion sources is the type of alternating current waveforms that are used to form and maintain a low temperature plasma. For DBDI, a sine or square waveform alternating current on the order of 10 kHz is typically used. However, the impact of the type of waveform on the power consumption and extent of energy deposited upon molecular ionization using DBDI sources has not been determined. Here, we report an active capillary DBDI source that generates a square wave plasma that requires less than $1 \mu\text{W}$ of power, which is over 100 times less than that of sine and triangular wave excitation to generate a comparable peak plasma voltage. Using square-wave excitation for DBDI-MS does not detrimentally affect the ion abundances for the detection of protonated dimethyl methylphosphonate (DMMP) or deprotonated perfluorooctanoic acid (PFOA) compared with sine and triangular waveforms.

Methods

A linear quadrupole mass spectrometer (LTQ XL, Thermo Fisher Scientific, San Jose, CA, USA) equipped with a custom ion funnel (Heartland Mobility, Wichita, KS, USA) and an active capillary dielectric barrier discharge ion source (Figure 1) was used for all mass spectrometry experiments. The DBDI source is similar to that used previously [8], except that the electrical circuit incorporates a linear power amplifier (500 kHz, 50 A peak; MP111 Apex, Australia) to enable the generation of a plasma using a square, sine, or triangular waveform. The DBDI source consists of quartz capillary (i.d. 1.50 mm, o.d. 1.60 mm, 2 cm in length) that is mounted on axis with the capillary entrance to the mass spectrometer [8]. The quartz capillary is surrounded by an outer Cu cylinder electrode (i.d. 1.7 mm, o.d. 2.5 mm, 1.5 cm in length). A

grounded stainless steel wire (0.30 mm in diameter) was inserted 0.75 cm into the quartz capillary. By application of a high-voltage AC field between the outer and inner electrodes (Figure 1), a DBD can be formed.

To generate square, sine, and triangular waveforms, a function generator (20 MHz; DG1022; Rigol, Beaverton, OR, USA) was connected to an amplifier (Figure 1). For all experiments, an input frequency of 10 kHz and amplitudes of 400 to 2000 mV were used. The amplifier output is connected to a custom transformer with a turn ratio of 6:1200 wound on a high-frequency ferrite core (TDK H7C4 Z; bandwidth higher than 150 kHz). The no-load peak output voltage of the transformer is approximately $\sim 6 \text{ kV}_{\text{p-p}}$. The input (V_1), amplified (V_2), and plasma (V_3) voltages were monitored using an oscilloscope (200 MHz, 4GS/s; WaveSurfer 3024; LeCroy, Chestnut Ridge, NY, USA), a differential probe (25 MHz; SI-9000; Sapphire Instruments, New Taipei City, Taiwan), and a high voltage probe (6 kV, 1000:1, 400 MHz, 50 M Ω ; PPE, LeCroy), respectively. The plasma current was obtained by measuring voltage across a low resistance, low inductance current sense resistor using an oscilloscope. The insertion of the current sense resistor has a marginal impact on the plasma current due to its low resistance and inductance. The measurement of voltage, V_3 , has essentially no impact on the measured current due to its high impedance but adds an additional load capacitance that may enhance the oscillations in the measured plasma current slightly, particularly with square wave excitation.

For DBDI-MS, molecules of interest were introduced by vapor pressure to the plasma source from sample solutions ~ 1 cm below the quartz capillary entrance of the ion source. The details of the thermometer ion experiments and data analysis are described in the Supporting Information [8].

Results and Discussion

The electrical circuit used to generate a continuous dielectric barrier discharge consists of a function generator, a power amplifier, and a high ratio transformer (Figure 1). The measured voltages (V_1 , V_2 , and V_3) and current (V_4/R , $R = 274 \Omega$) versus time using square, sine, and triangle waveform excitations are shown in Supplementary Figure S1. The average power of the plasma was obtained from the plasma voltage and current measurements using Supplementary Equation S1. The amplifier gain is 10 and the transformer turns ratio is 1:200. For example, a square wave input voltage (V_1 ; Supplementary Figure S1) of 600 mV resulted in an amplified voltage of ~ 6 V applied to the primary winding (V_2 , Supplementary Figure S1). For this voltage, the peak plasma voltage was transformed with a maximum value of ~ 1.3 kV ($\sim 2.5 \text{ kV}_{\text{p-p}}$), resulting in a maximum plasma current of 800 μA (Supplementary Figure S1). For the sine and triangular waveforms, more than twice the input voltage was required to produce a similar peak plasma voltage to that obtained using of the square waveform. Moreover, the power consumed by the square waveform (0.8 μW) was more than 100 times lower than that for the sine (106 μW) and triangle (287 μW) waveforms.

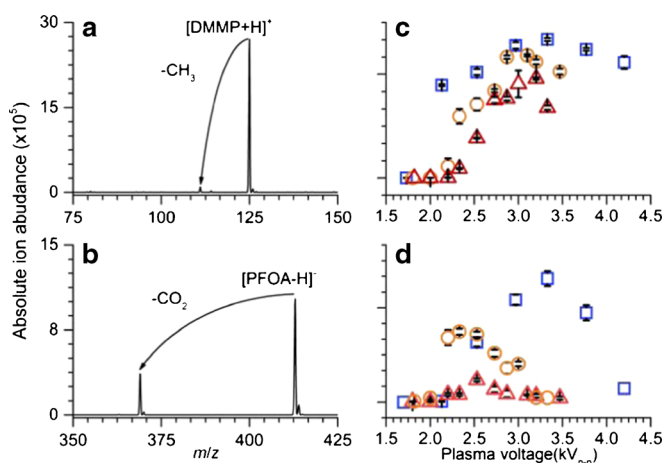


Figure 2. Dielectric barrier discharge ionization mass spectra of test analytes: (a) dimethyl methylphosphonate (DMMP; positive mode) and (b) perfluorooctanoic acid (PFOA; negative mode). Abundances of (c) $[\text{DMMP} + \text{H}]^+$ and (d) $[\text{PFOA} - \text{H}]^-$ versus plasma voltage for square (squares), sine (circles), and triangular (triangles) excitation

There are two primary operating modes of DBD referred to as filamentary and homogeneous. Filamentary DBDs result in the random, irregular formation of transient microdischarges. Homogeneous plasmas are characterized by regularly occurring transient microdischarges every half waveform cycle. For triangle and sine wave excitation operated at 3.0 and 2.7 $\text{kV}_{\text{p-p}}$, measured current spikes that are over 100% higher than the average current occur every half cycle (Supplementary Figure S1). The triangle waveform plasma also results in the measurement of additional irregular current spikes (Supplementary Figure S1). For square wave excitation, current spikes of such magnitude were not observed for plasma voltages $< 2.5 \text{ kV}_{\text{p-p}}$ (Supplementary Figures S1 and S2). For higher voltages, regular plasma spikes occur every half cycle that have full-width half max values of $\sim 700 \text{ ns}$ (Supplementary Figure S2), which are significantly longer than the resolution of the oscilloscope (4 ns). These data indicate that the triangle waveform plasma exhibits filamentary characteristics, and the sine- and square-wave plasmas are more homogeneous. A key distinction of square-wave excitation is that at similar plasma voltages for optimal ion detection (vide infra), the magnitudes of plasma current spikes are over $100\times$ lower than for sine and triangle excitation.

For squarewave DBDI operated in homogeneous mode, there is a significant overshoot oscillation for the plasma voltage (V_3) and current for the square wave compared with the signal and amplified voltages (V_1 and V_2 ; Supplementary Figure S1). For example, within each half cycle ($\sim 30 \mu\text{s}$), the maximum and minimum plasma voltage values vary between near zero and an absolute maximum peak voltage of $\sim 1.3 \text{ kV}$. This can be attributed to oscillations at the resonant frequency of the resonant circuit formed between the parasitic winding capacitances and the leakage inductances of the transformer [14]. These are excited by the stepped voltage waveforms. In the future, the transformer will be fabricated to minimize leakage inductance, parasitic capacitance, and maximize coupling between the primary and secondary winding.

The effect of the plasma waveform on the performance of DBDI-MS was investigated. Sampling the vapor headspace of a solution containing DMMP ($\sim 150 \text{ ng}$ in $100 \mu\text{L}$ methanol) using a square waveform resulted in the formation of an ion at m/z 125 corresponding to protonated DMMP in relatively high abundance ($\sim 2.5 \times 10^6$ ion counts; Figure 2). Collisional activation of protonated DMMP can result in the primary neutral loss of a methyl group [9]. Under these conditions, methyl group loss was minimal ($< 5\%$). For square-wave ionization, the optimal abundance of $[\text{DMMP} + \text{H}]^+$ was obtained by use of a plasma voltage of $\sim 3.4 \text{ kV}_{\text{p-p}}$. The maximum ion abundances obtained with sine and triangular waveforms were slightly lower than that obtained by use of the square waveform (Figure 2).

For negative mode, DBDI-MS of the vapor headspace of a PFOA solution ($\sim 480 \text{ ng}$ in $100 \mu\text{L}$ methanol) resulted in the formation of an ion at m/z 413 corresponding to $[\text{PFOA} - \text{H}]^-$ ($\sim 9 \times 10^5$ ion counts; Figure 2) and a relatively abundant ion at m/z 369. The latter ion corresponds to decarboxylated $[\text{PFOA} - \text{H}]^-$ owing to ion activation in the ion source and/or during transmission of the ions to the mass analyzer. Using the square waveform, the plasma voltage for optimal abundance of intact $[\text{PFOA} - \text{H}]^-$ was $\sim 3.5 \text{ kV}_{\text{p-p}}$ compared with $\sim 2.5 \text{ kV}_{\text{p-p}}$ for sine and triangular waveforms. The extent of $[\text{PFOA} - \text{H}]^-$ fragmentation was slightly lower ($\sim 30\%$ dissociated; Figure 2) using a square waveform than for sine (43%) and triangle (44%) waveforms at their optimal input voltages under these conditions. The extent of dissociation of $[\text{PFOA} - \text{H}]^-$ ($\sim 30\%$) obtained here is comparable to that reported by use of a different type of

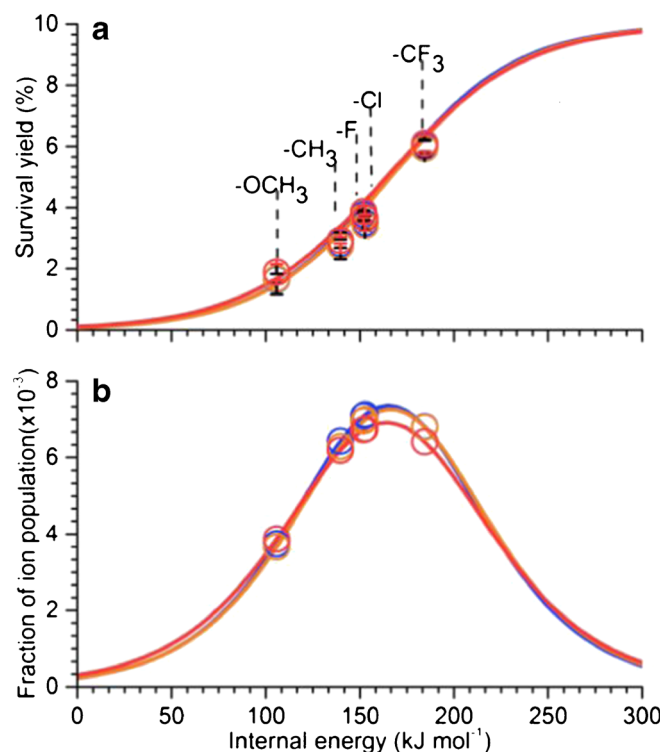


Figure 3. (a) The breakdown curve and (b) internal energy distributions of the thermometer ions obtained using square (blue), sine (orange) and triangle (red) wave DBDI using a plasma voltage of $2.5 \text{ kV}_{\text{p-p}}$, $2.7 \text{ kV}_{\text{p-p}}$, and $3.0 \text{ kV}_{\text{p-p}}$

dielectric barrier discharge ion source (~20%) [15]. The optimal ion abundances of [PFOA – H]⁺ obtained by a square waveform were significantly higher than by use of the triangle and square waveforms. These results collectively indicate that there are no apparent detrimental effects of using a square waveform on the ion signal of DBDI-MS in comparison to using sine or triangular waveforms under these conditions.

To investigate the extent of energy deposition using the three different excite waveforms, the “survival yield” method [16] and benzylammonium thermometer ions [8] were used. The relative extent of fragmentation of 4-methoxy benzyl ammonium (–OCH₃), 4-methyl benzyl ammonium (–CH₃), 4-fluoro benzyl ammonium (–F), 4-chloro benzyl ammonium (–Cl), and 4-trifluoromethyl benzyl ammonium (–CF₃) is plotted as a function of bond dissociation energy (Figure 3), which were calculated and benchmarked to experimental data as described in a previous study [8]. A plasma voltage of ~2.5 kV_{p-p} was used for the square waveform compared with values of ~2.7 and ~3 kV_{p-p} for the sine and triangle waveforms, respectively. For the square waveform, protonated 4-substituted benzylamines could not be detected in appreciable abundance using a plasma voltage of ~6.0 kV_{p-p}, presumably owing to significant degradation of the precursor and product ions. The derivative of the breakdown plot yields the corresponding internal energy distributions of the ions (Figure 3). The shape and median of the internal energy distributions obtained by use of a square, sine, and triangle waveform DBDI mass spectrometry are essentially identical. These data are consistent with the mechanism of ionization resulting from the use of a square waveform being similar to that for sine and triangular wave excitation.

A modular active capillary DBDI circuit was designed using an H-bridge and transformer (Supplementary Figure S3) and used to power active capillary DBDI using a 9 V battery (PP3). Based on the measured power consumption of the plasma, H-bridge, and transformer, active capillary DBDI can be powered continuously for 12 h despite a ~75% power loss from the prototype transformer (Supplementary Figure S3).

Active capillary DBDI using a square waveform can yield significant performance gains in terms of reducing the power consumption by over 100× compared with sine and triangle waveform excited plasmas. Square-wave DBDI can be used to detect protonated DMMP and deprotonated PFOA in comparable or higher abundances than with sine and triangle wave plasmas. For a given plasma voltage, the use of a square waveform excitation can be a significantly “harsher” ion source than by using a sine or triangle waveform as determined by benzylammonium thermometer ions. However, at “optimal” plasma voltages for ion detection, the extent of energy deposited is essentially identical in DBDI mass spectrometry for square, sine, and triangle wave plasmas. The square-wave active capillary DBDI has the advantages that the plasma power consumption can be exceedingly low (<1 μW) and intact ions with low bond dissociation energies (~105 kJ mol⁻¹) can be detected with minimal fragmentation. Moreover, the ion source is compact and no compressed gases or fluid pumps are required. With a transformer optimized to reduce core loss, this portable ion

source can be powered continuously using a common 9 V battery for over ~50 h for trace chemical analysis by mass spectrometry. Square-wave active capillary DBDI should significantly benefit portable ion detection devices for the rapid detection of thermo-labile compounds, such as chemical warfare agents, persistent organic pollutants, and explosives.

Acknowledgments

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