Filament control for a highly reproducible electron-activated dissociation (EAD) device

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ABSTRACT

We developed a filament calibration strategy, which ensures safe, efficient and reproducible operation of electron-activated dissociation (EAD). Reproducibility and efficiency are demonstrated for both singly charged precursor ion at kinetic energy (KE) 10eV and doubly charged precursor ion at near zero kinetic energy

INTRODUCTION

Alternative fragmentation technology often generates more informative spectra than conventional collision-induced dissociation (CID). However, in the past, 3 issues hampered its widespread adoption: fragmentation inefficiency, lack of reproducibility, difficulty of operation and low mass spectrometer sensitivity. EAD, which has recently been commercialized on the ZenoTOF 7600 system, demonstrated improvements on each of these 3 challenges. Previous reports focused on the innovations responsible for the improved mass spectrometer sensitivity and EAD fragmentation efficiency.[1] In this work, we report a novel filament calibration strategy aimed at improving reproducibility and ease of use.

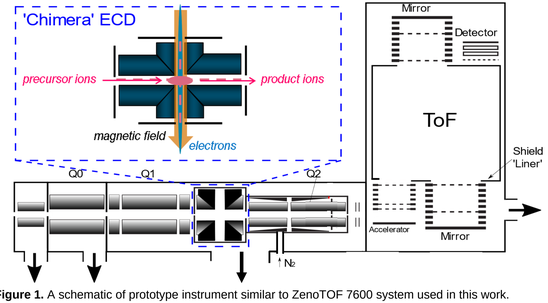

Figure 1. A schematic of prototype instrument similar to ZenoTOF 7600 system used in this work.

MATERIALS AND METHODS

All experiments were performed on a prototype ZenoTOF 7600 system equipped with a branched-rf EAD cell. Triacetyl-β-cyclodextrin and reserpine were used to assess reproducibility of EAD fragmentation. Electron capture efficiency was monitored for both ECnoD (electron capture no dissociation) process of $[M+2H]^{2+}$ triacetyl-β-cyclodextrin at kinetic energy(KE) of 1 eV and ECD process of $[M+3H]^{3+}$ of neurotensin at 0eV was used for electron capture efficiency monitoring . A measurement jig was developed for measuring emission and collection currents at the emitting filament and adjacent lenses. A software capability for detection of emission current saturation was developed based on the observed inflexion point in the emission graph.

Conventional control

Conventionally, filament emission is controlled either by adjusting the drive voltage or current or by using feedback loop controllers for emission current control. Adjusting the drive voltage or current is problematic because the operation range is narrow and differing for each filament (Figure 3 top).

Direct use of feedback loop controllers is not particularly suitable for applications operating at both low and high electron kinetic energies. Electron emission at strong electron currents required for good EAD performance is space-charge saturated, which couples electron kinetic energy and filament emission (Figure 3 bottom). This limits the strength of the emission currents that can be used without damaging filaments.

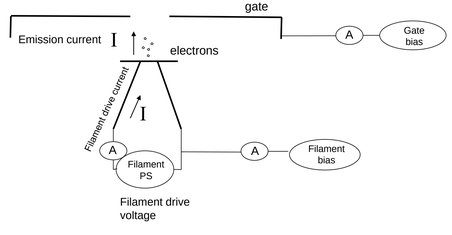

Figure 2: Schematic of the filament and gate electrical circuits.

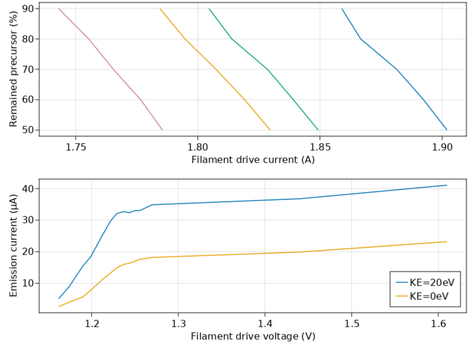

Figure 3: Electron capture efficiency dependency on filament drive current measured under identical experimental conditions for different filaments for neurotensin 3+ ion, where y-axis represents remaining unreacted precursor (top). Emission current dependency on filament drive voltage at different kinetic energies measured at emission filament.

Proposed calibration strategy

In this work, we propose a calibration strategy, which maps the electron emission at fixed kinetic energy to the filament drive voltage. For this we leverage a property that filament emission exhibits a near perfect linear relationship between filament drive voltage and emission current upon reaching saturation point (Fig 4). This offers a safe strategy to detect electron beam current saturation point and calibrate safe operating range (Fig. 5).

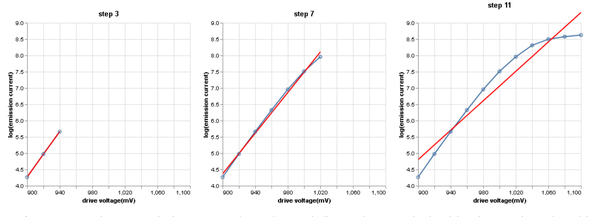

Figure 4: An electron emission current dependency similar to the one obtained in Figure 3 is replotted in log(emission current) domain. Measurement is performed at gate electrode at KE=0eV. Left panels shows only data until space charge saturation is reached, exhibiting near perfect linear fit. The right panel shows data beyond saturation point, where the curve changes its shape. Middle point shows data and its linear fit prior to saturation point with the saturation point being included.

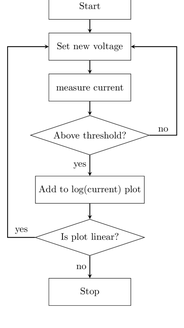

Figure 5: A workflow for filament calibration procedure.

Figure 6 shows that the described strategy has superior instrument to instrument reproducibility compared to controlling the filament via drive current adjustment.

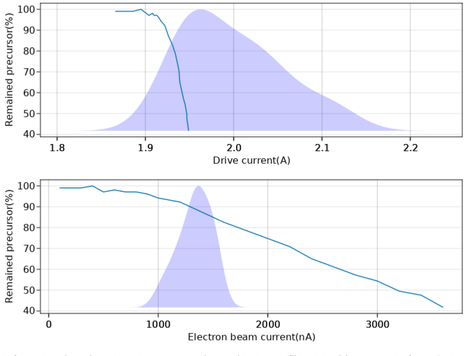

Figure 6 (top): Exemplar electron capture rate dependency on filament drive current for ECnoD reaction of $[M+2H]^{2+}$ triacetyl-β-cyclodextrin at kinetic energy(KE) of 1 eV with overlayed distribution for drive corresponding to 10% precursor consumption measured for 5 instruments (10 filaments). **Figure 6 (bottom):** Data from the same experiment plotted where similar dependency is plotted against electron beam current measured at gate electrode.

CONCLUSIONS

Conventional filament operation is challenging for low electron energy applications such as ECD with an instrument-to-instrument variability making it necessary to use electron-ion reaction for tuning purposes.

Proposed calibration strategy provides safe and efficient means to control the filament and yield reproducible results.

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