Windowless Miniature Spark Discharge Light Sources for Efficient Generation of VUV Radiation Below 105 nm for On-Capillary APPI (CAPI)

Hendrik Kersten; Klaus J. Brockmann; Rob O´Brien; Thorsten Benter

Physical & Theoretical Chemistry
Wuppertal, Germany
Institute for Pure and Applied Mass Spectrometry

Introduction

Overview:

Common Atmospheric Pressure Photoionization (APPI) radiation sources make use of windows to seal the VUV generating discharge region from the remaining MS environment. This is mainly done to prevent the discharge being perturbed or quenched. However, any window material used for VUV transmission leads to:

→ **restriction of transmission above the optical cutoff** (e.g., LiF: 105 nm)
→ **severe reduction of transmission efficiencies above the cutoff**

Challenge:

Design of a stable and efficient VUV radiation source without the need of window material.

Approach:

Spark discharges within apertured, intersecting capillary assemblies. Pressure balanced separation is used for sustained stable VUV emissions.

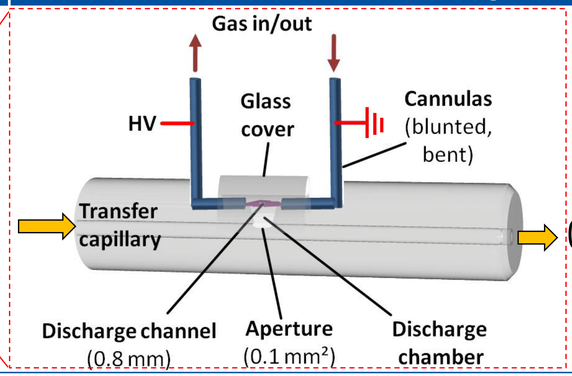
Methods

MS	Bruker esquire6000 quadrupole ion trap and a Bruker micrOTOF orthogonal time of flight MS, both equipped with home-built laminar flow ion sources (LFIS) for sample delivery
Radiation source	Home-built spark discharge lamps
Discharge gases	Helium, Argon and mixtures of both
Power supply	Custom designed DD20_10 C-Lader (Hartlauer Präzisionselektronik GmbH, Grassau, Germany)
Spectroscopy	VM 200 VUV monochromator (Resonance, Ltd. Barrie, On, Canada)
Gas phase samples	For LOD determination: Gas phase sampling from a large volume photoreactor (1080 L) with gradual enrichment of the analyte
Chemicals	Benzene, 2-butanone

CAPI: Principle of Operation

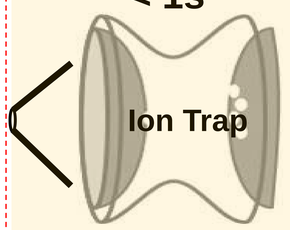
- High **spark** frequency in up to 1 atm continous discharge gas flow; line emission; „cold“ operation
- **NO window** between the area of VUV generation and the sample gas flow
- **Pressure balanced separation** of the discharge chamber ($p_{discharge}$) and the analyte gas stream (at static pressure p_{static})
- Two **ionization modes**:
  - ($p_{discharge}$) = (p_{static}) → ***VUV***
  - ($p_{discharge}$) > (p_{static}) → ***VUV + Metastables (Penning)***

Experimental Setup

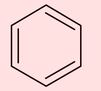


Temporal Resolution:

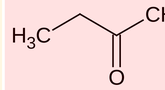
< 1s



Limits of Detection (3σ)

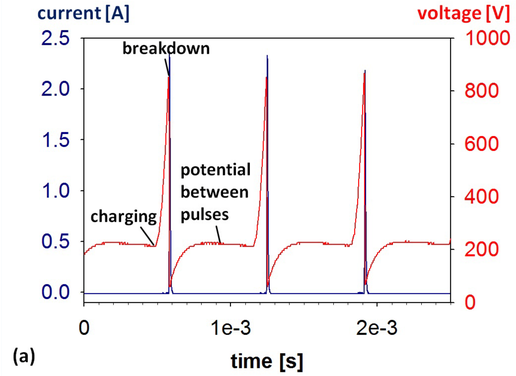


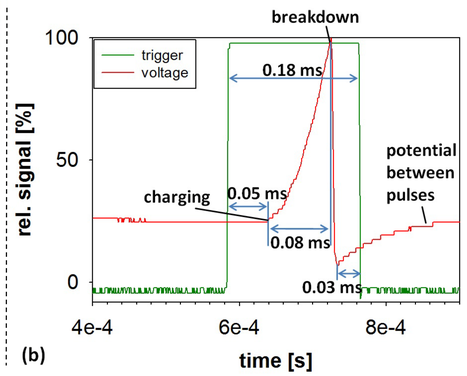
0.5 ppbV

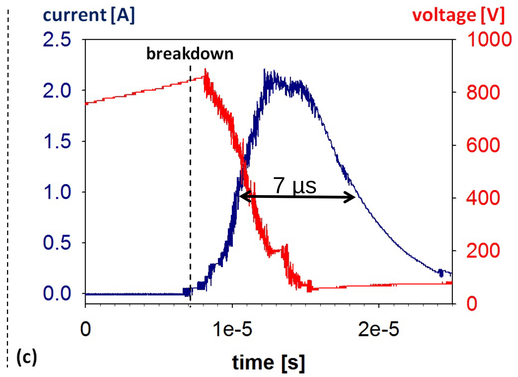


0.1 ppbV

Current, Voltage and Trigger Characteristics







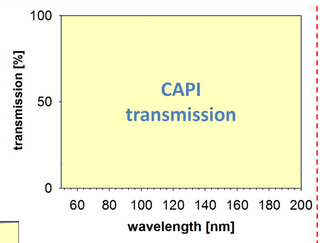
(a) Temporal correlation of the current and voltage evolution, illustrated by three subsequent breakdowns

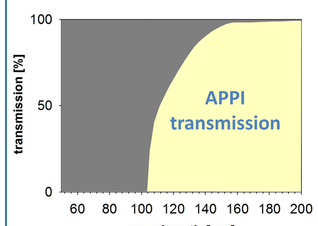
(b) Temporal correlation of the trigger signal and the potential on the cathode

(c) Temporal evolution of the voltage and current during one spark

VUV Transmission: APPI vs. CAPI

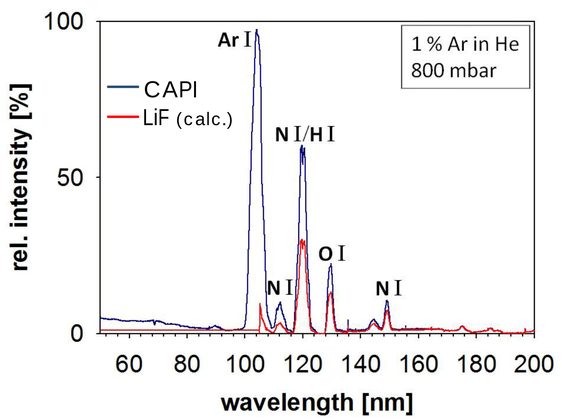
right: Windowless operated CAPI source:100 % transmission of any generated radiation into the sample gas flow.

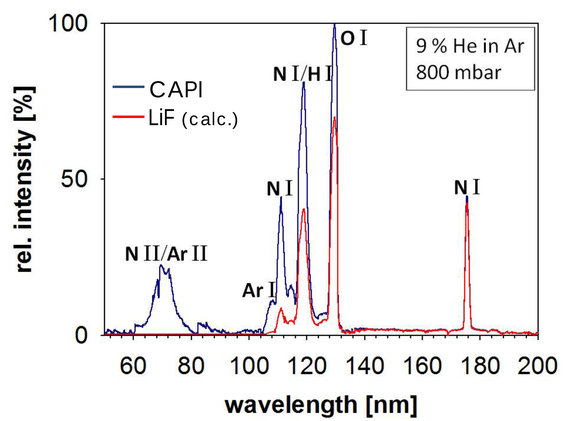




left: Transmisson restrictions due to LiF windows commonly used for APPI sources. The optical cutoff is located at 105 nm.

VUV Emission of Different Discharge Gas Compositions with CAPI





Conclusions

- **CAPI is a novel photoionization source operated windowless**
  - → high frequency of sparks
  - → medium to atmospheric pressure in the discharge region
  - → continuous discharge gas flow (100 -500 mL/min)
  - → cold discharge
  - → line emission
  - → high photon flux on a small illuminated area
  - → high temporal and spatial discharge stability
  - → ionization via VUV radiation and metastables (Penning ionization) possible
- **CAPI is a cost efficient and powerful ion source**
- **CAPI allows for flexible discharge gas selection and thus flexible ionization characteristics**
- **Future aspects:**
  - → systematic investigations on discharge gas composition and attainable radiation/metastable formation
  - → systematic investigations on the correlation between the UV/VIS spectra, the discharge chemistry and the VUV generation/ metastable formation

Literature

1) Kersten, H. *Development of an Atmospheric Pressure Ionization source for in situ monitoring of degradation products of atmospherically relevant volatile organic compounds*, Dissertation, Bergische Universität Wuppertal, Wuppertal, **2011**; urn:nbn:de:hbz:468-20110418-092806-6
2) Kersten, H.; Derpmann V.; Barnes, I.; Brockmann, K. J.; Benter, T.; O ´ Brien, R. *A novel APPI-MS setup for in situ degradation product studies of atmospherically relevant compounds: Capillary Atmospheric Pressure Photo Ionization (CAPI)*, to be published **2011**.
3) Korth Kristalle GmbH *VUV-Transmissionsspektrum von LiF*, **2010**; http://www.korth.de/de/503728952d091450d/503728952d0b33731.htm
4) Ralchenko, Y.; Kramida, A. E.; Reader, J.; NISTASDTeam(2008) *NIST Atomic Spectra Database (version3.1.5)*, **2008**; http://physics.nist.gov/asd3.
5) Druyvesteyn, M. J.; Penning, F. M. *The Mechanism of Electrical Discharges in Gases of Low Pressure* Reviews of Modern Physics **1940, 12, 87.**

Acknowledgement

Financial support of this work by the German Research Foundation (DFG) within project POXSA (BE 2124/4-1) is gratefully acknowledged. The authors thank Resonance Ltd., Barrie, On, Canada for collaboration on VUV measurements.