



# Degradation of amoxicillin in water treated with DBD plasma

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# Outline

- Introduction to my STSM
- Motivation
- Experimental setup
- Diagnostic methods
- Results
- Summary
- Next step

# COST TD1208

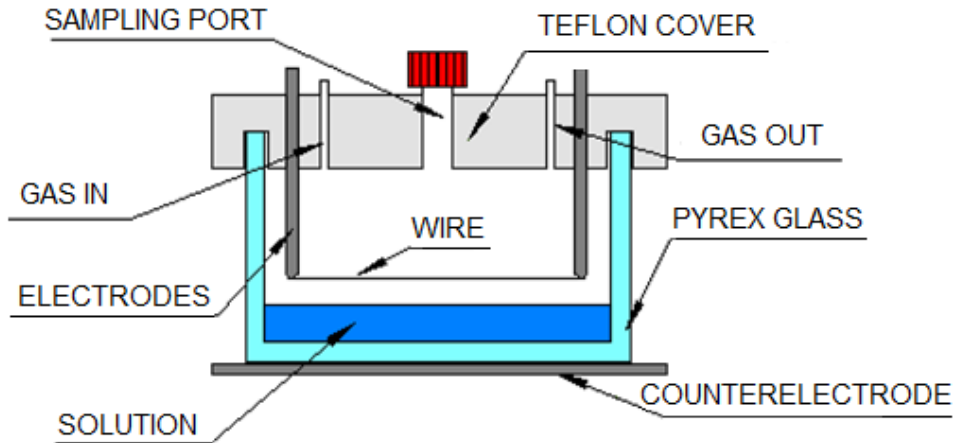
## „Electrical Discharges with Liquids for Future Applications”

- 3 weeks of Short-Term Scientific Missions (STSM) at Department of Chemistry University of Padova, Italy
- Purpose of STSM was to use Non thermal plasma DBD discharge to degrade amoxicillin solution
- Learn HPLC/MS analysis from experienced team of prof. C. Paradisi

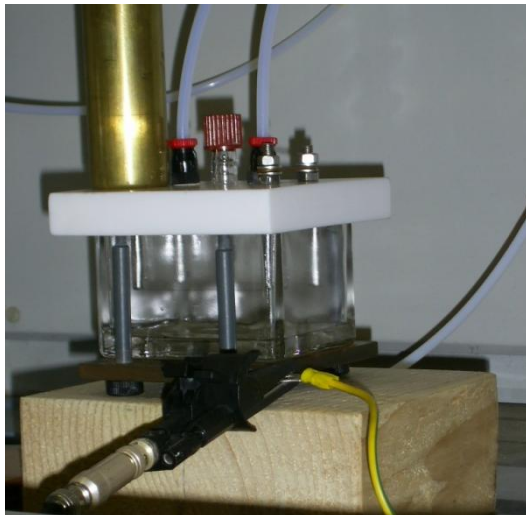
# Motivation

- Amoxicillin is one of the main antibiotics polluting the waters
- Can DBD discharge degrade amoxicillin?
- If yes, what is the mechanism/kinetics?

# Experimental set up

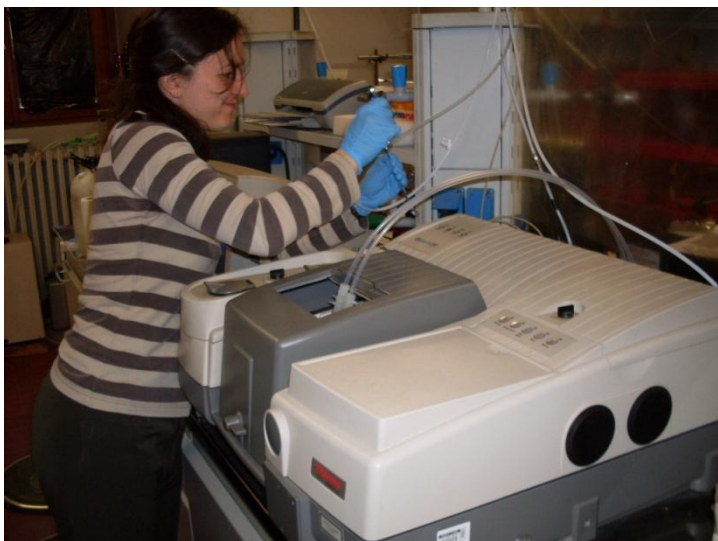


- Glass reactor (95x75x60 mm)
- Power supply: AC (50 Hz; 16-18 kV)
- 2 parallel wires (0.15 mm diam., 73 mm length, 38 mm one to other)
- Distance wire - solution: 15 mm
- Volume of treated solution: 70 mL



# Diagnostics: HPLC and FTiR

- Pump system P2000 Spectra System and diode detector UV6000LP
- Eluents:
  - 99:1 H<sub>2</sub>O and acetonitrile plus phosphate buffer (20 mM) with pH of 2.2
- Column used:
  - Zorbax SB-Aq



- FTiR spectrometry using NICOLET 5700
  - CO<sub>2</sub> band at 2340 cm<sup>-1</sup>
  - Humid air flow passing through the reactor at 30 mL/min

# Mass Spectrometry



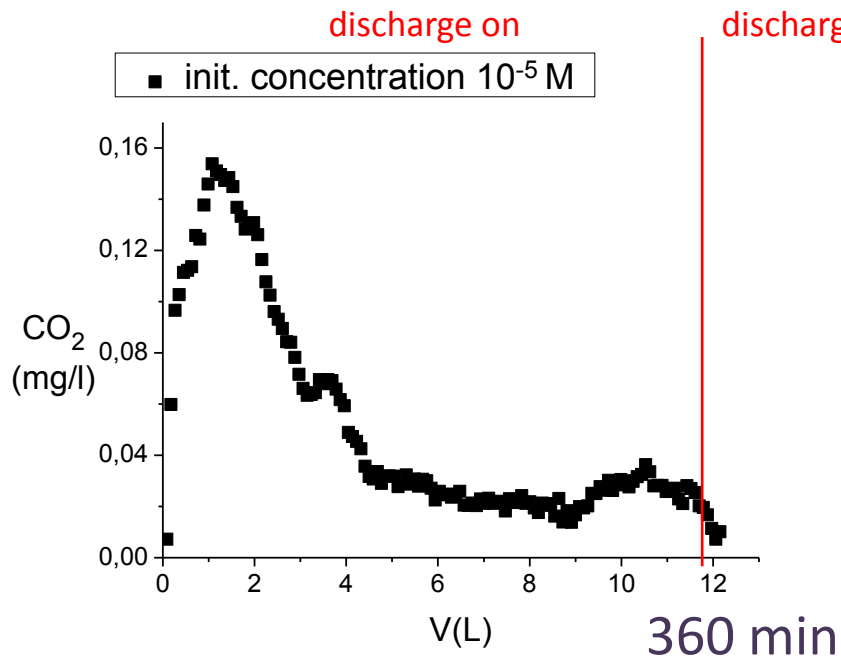
- Positive polarity
- N<sub>2</sub> dry gas temperature 350°C
- N<sub>2</sub> 10 L/min
- Capillary voltage 4000 V
- Eluents:
  - Acetonitril + 0.1% formic acid
  - H<sub>2</sub>O + 0.1% formic acid
  - Gradient from 5% to 100% in 20 min
- Column used:
  - Gemini C18 150 x 4.6



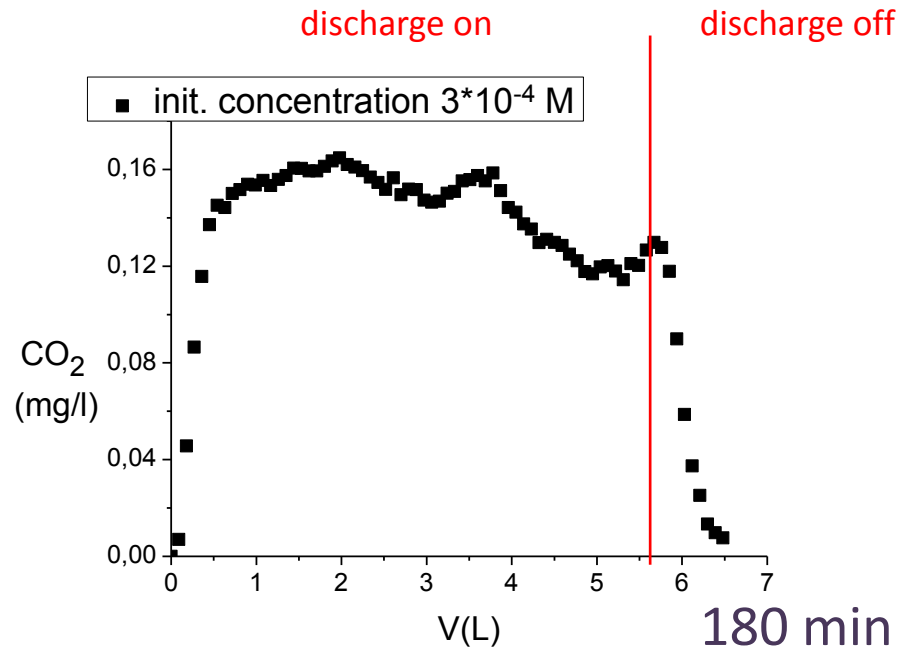
Agilent Technologies mass spectrometer with ion trap MSD Trap SL model G2245D with ESI and HPLC series 1100 with binary pump model G1312A

# RESULTS

## CO<sub>2</sub> measurement



100 % of carbon mass emitted

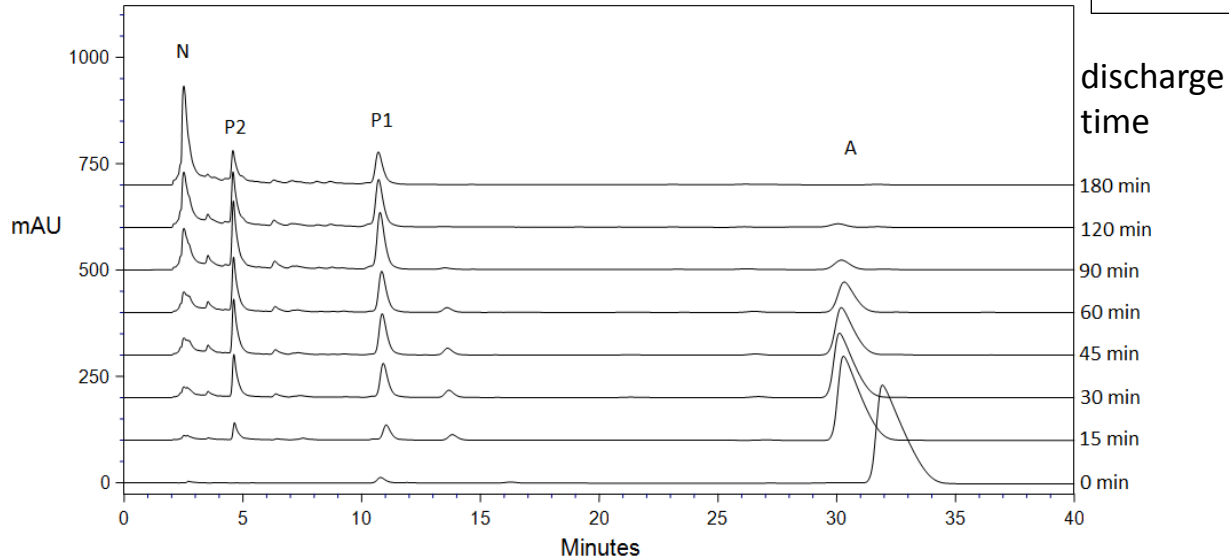


5 % of carbon mass emitted



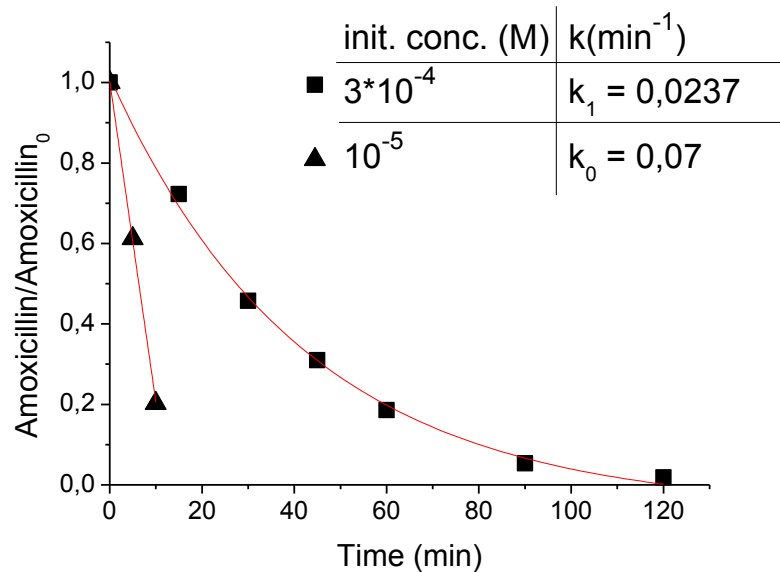
# HPLC results

Init. concentration  $3 \cdot 10^{-4}$  M



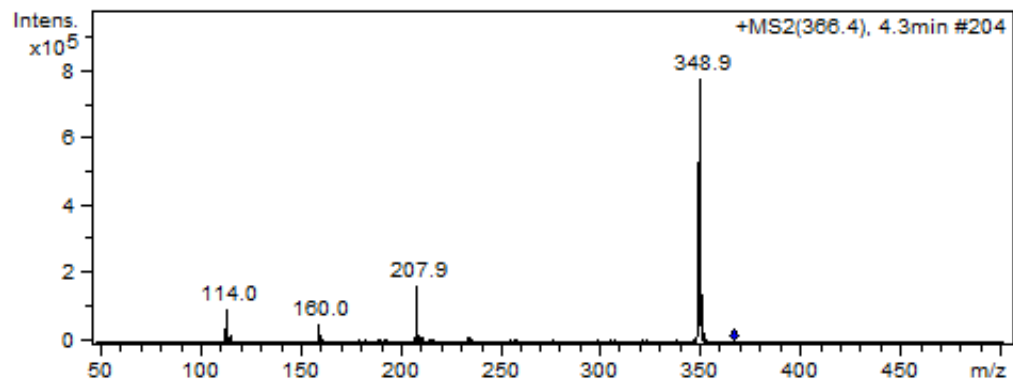
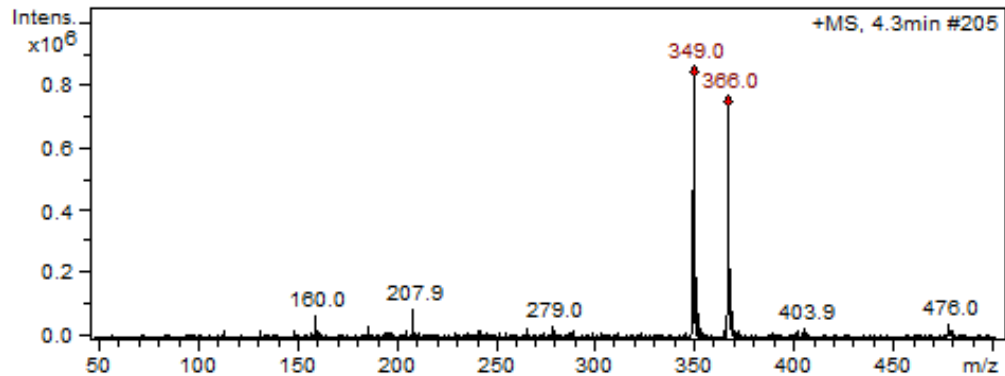
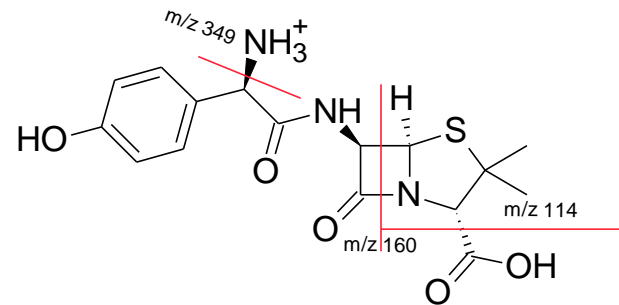
A – Amoxicillin  
 P1 – Degradation product 1  
 P2 – Degradation product 2  
 N – Nitric acid

**HPLC chromatogram of amoxicillin degradation**



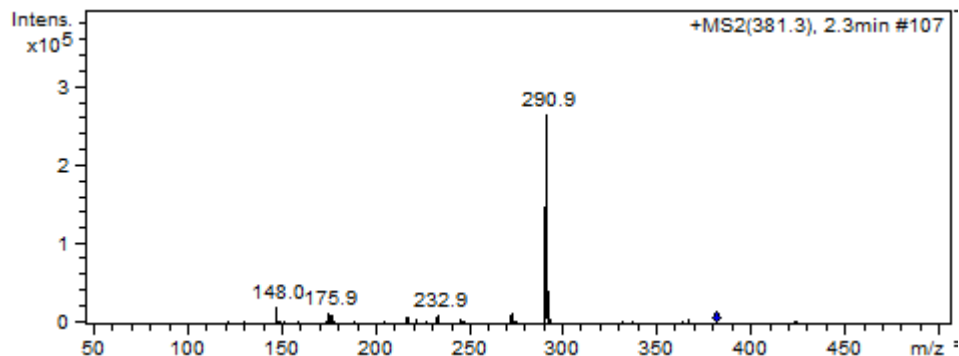
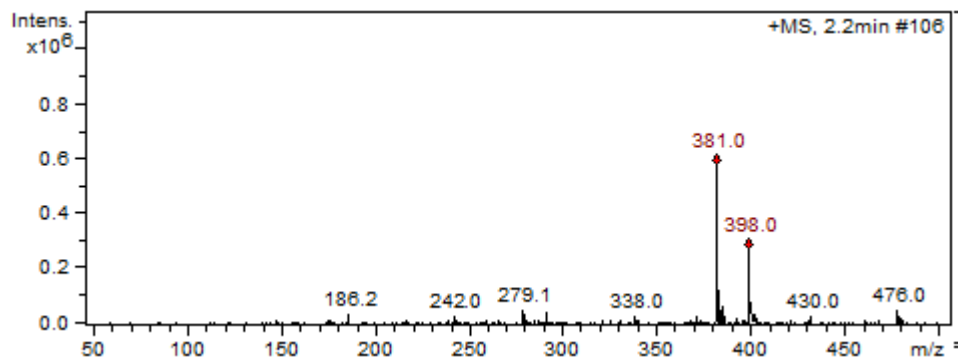
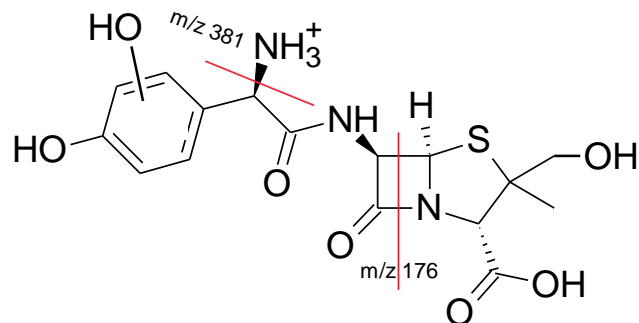
**Degradation of amoxicillin and reaction constants**

# Amoxicillin MS



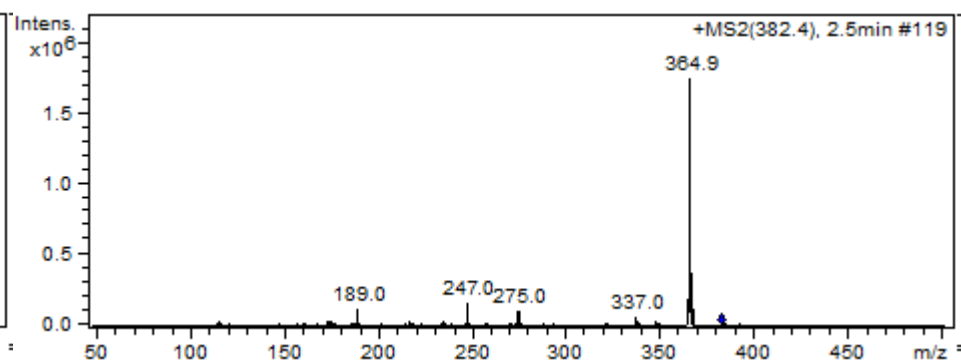
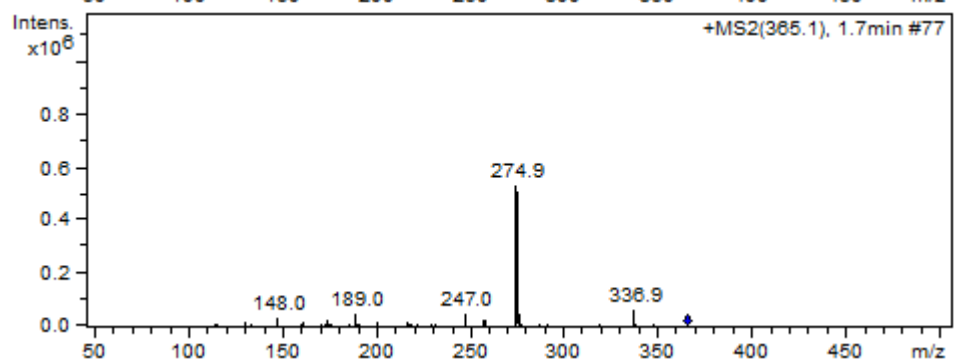
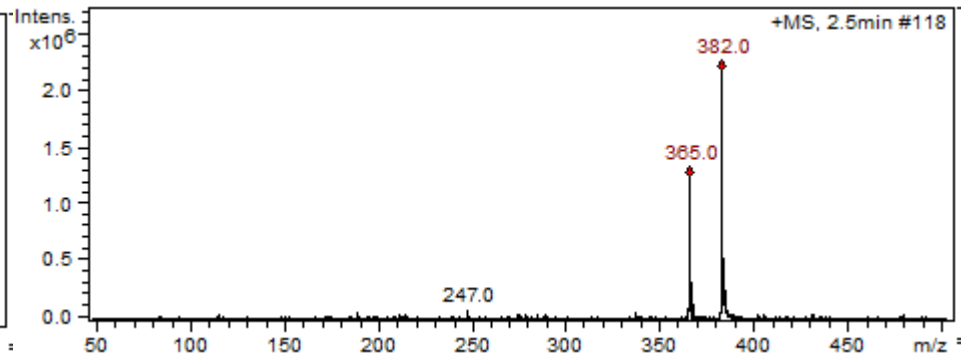
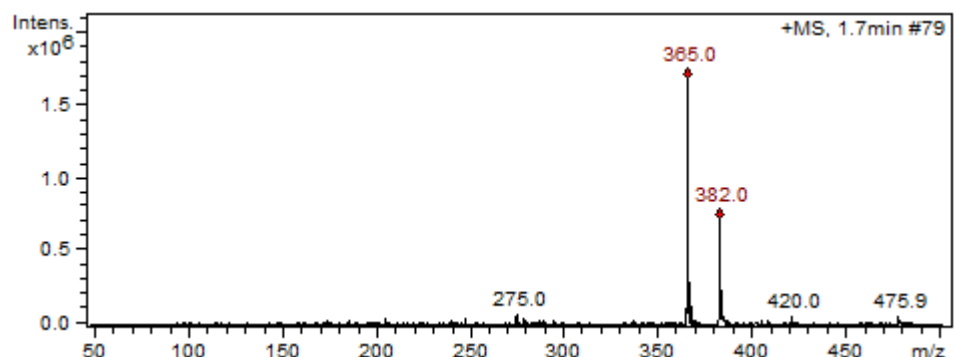
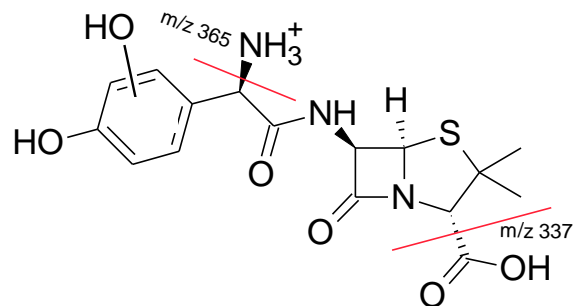
Amoxicillin and fragmentation spectra at retention time of 4.1 min

# P2 amoxicillin product



Degradation product P2 eluted with retention time of 2.2 min is a di-hydroxylated product of mass 398  $m/z$ .  
 A possible structural attribution is shown

# P1/P3 amoxicillin products



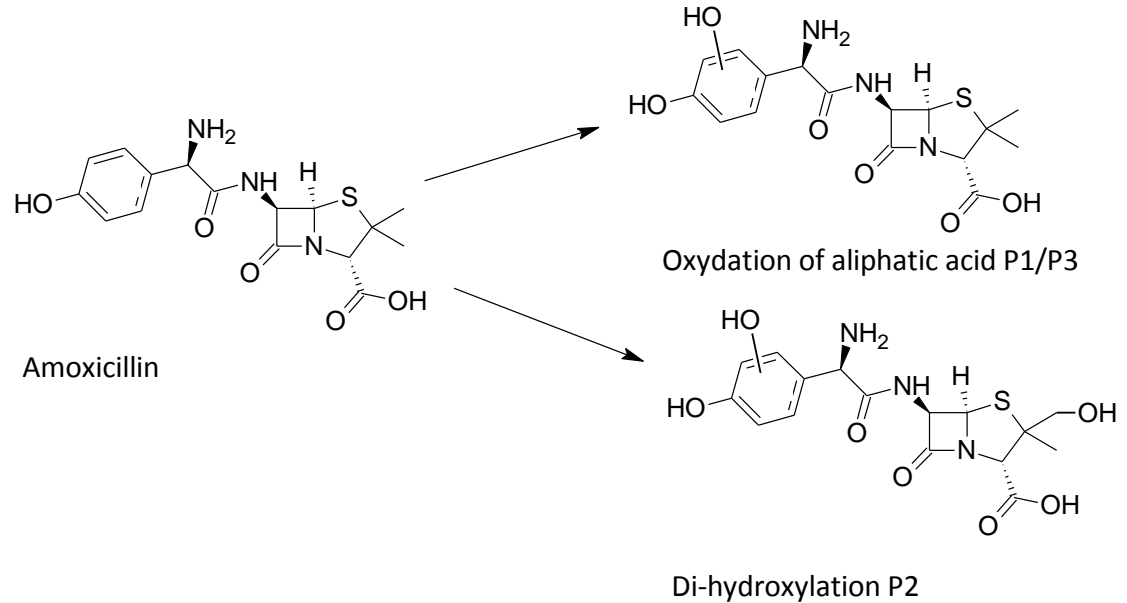
Degradation products P1 and P3 eluted with retention times of 1.7 and 2.5 min, respectively.

Oxidation of aliphatic acid in two different positions amoxicillin of mass 382 m/z

# Summary

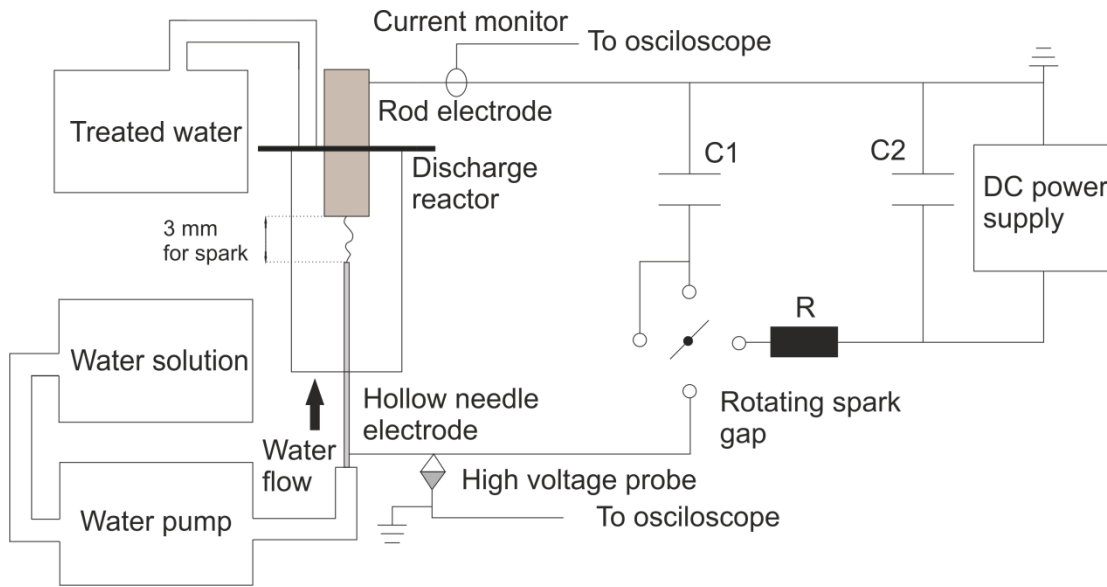
## DBD discharge degradation of amoxicillin

- Degradation rate constant is higher when the initial concentration is lower
- Can achieve 100% degradation but degradation fragments still remain
- CO<sub>2</sub> is one of the products



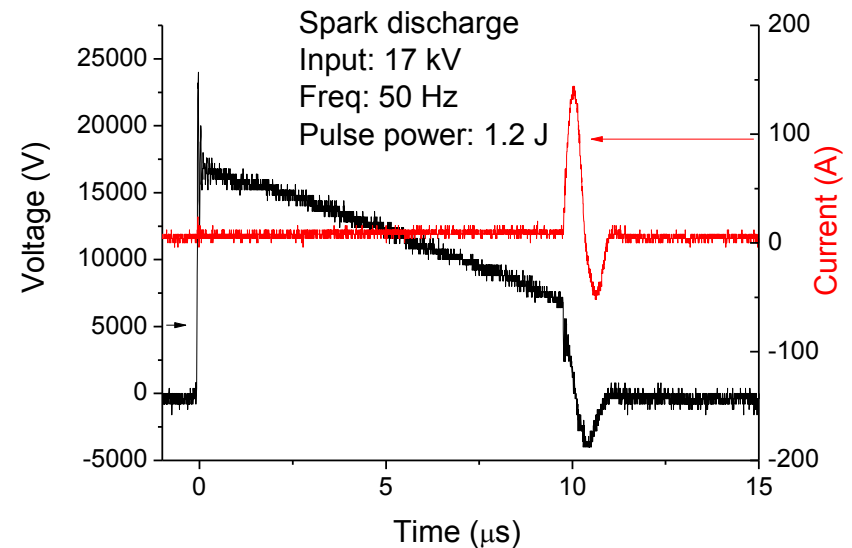
#	Retention time (min)	MS fragments (m/z)	Observations
1	1.7	148; 189; 247; 274; 337; 365; 382	Identified as P1
2	2.2	148; 176; 233; 291; 370; 381; 398	Identified as P2
3	2.5	148; 189; 247; 274; 337; 365; 382	Identified as P3
4	4.3	114; 160; 208; 366; 388	Amoxicillin (A)

# Spark in water



## REACTOR PARAMETERS:

- Cylindrical reactor made of PTFE
- Inner diameter: 25 mm
- High voltage electrode -> Stainless steel hypodermic needle, inner diameter: 1.6 mm
- Outer diameter: 2 mm
- Grounded electrode -> Stainless steel rod, diameter: 5 mm
- Gap between the electrodes: from 3 mm
- Water flow 30 ml/min



# HPLCMS triple quadrupole

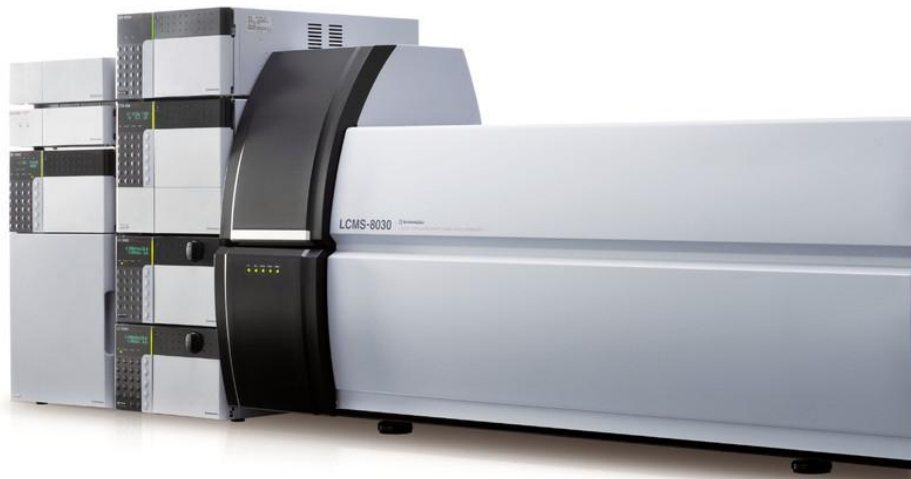
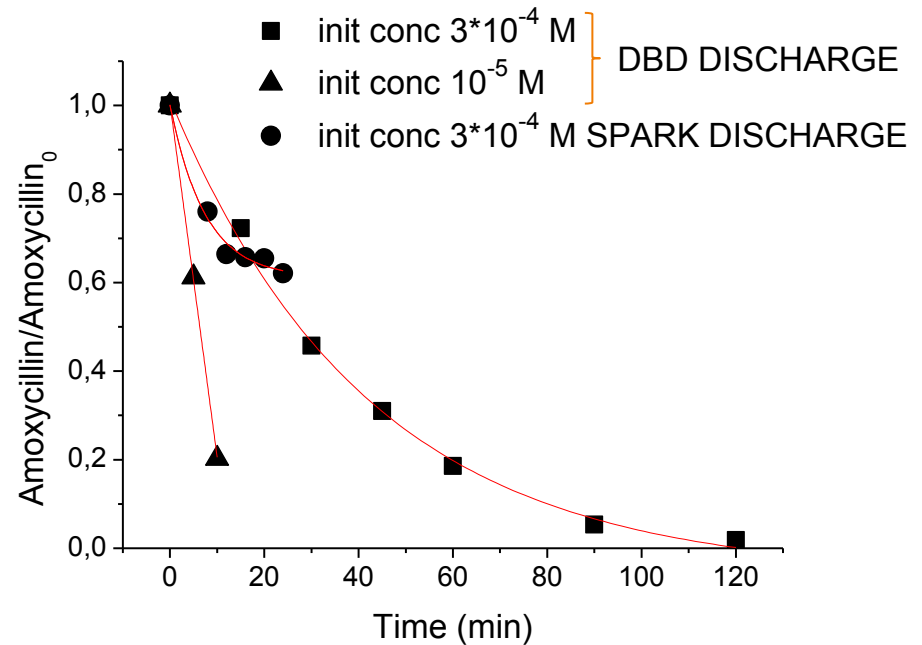
➤ Shimadzu LCMS-8040

➤ Eluents:

- Acetonitril + 0.1% formic acid
- H<sub>2</sub>O + 0.1% formic acid
- Gradient from 5% to 95% in 10 min

➤ Column used:

- Kinetex C18



- Q3 SIM for 366 m/z
- At retention time 1.6 min