Photoionization Interest Group Workshop Report

"Future needs of photoionization mass spectrometry for complex mixture analysis"

71th ASMS Conference on Mass Spectrometry and Allied Topics, Houston, TX

June 7, 2023

Organized by:

Luke Hanley (University of Illinois at Chicago, United States)
Christopher Rüger (University of Rostock, Germany)

Approx. Attendance: 20

The workshop began with the workshop chair, Christopher Rüger, presenting some introductory slides on complex mixtures, the diversity of ionization schemes and photoionization in general. Three experts were chosen to present a part of their research work and to lead the discussion on a diversity of topics in photoionization mass spectrometry. Particularly young scientists have been considered to give them an ideal platform for presenting their work with a strong interactive discussion character.

- **Prof. Janne Jänis** from the University of Eastern Finland (Joensuu, Finland) presented on the "Importance of photoionization in "biopetroleomics" and related studies". After briefly recapturing the basics of ionization coverage (chemical space: polarity versus molecular weight) and typical ionization reactions involved in (+/-)APPI, Prof. Janne outlined the usage of APPI for the analysis of highly complex biomass-based pyrolysis oils. The complementary character in comparison to ESI was pointed out utilizing common petroleomics data visualization strategies, such as O/C versus H/C (Van-Krevelen) diagrams. Moreover, he referred to the usage of APCI as an additional complementary technique for covering a larger chemical space. For APPI the high potential for application in (plant) metabolomics, *e.g.*, conifer needle extracts, was discussed.

- **Patrick Müller,** a PhD student from the University of Geneva (Geneva, Finland) from the group of Prof. Gérard Hopfgartner, presented on "Determining Double Bond Positions of Lipids using Supercritical Fluid Chromatography Photoionization Mass Spectrometry and Collision-Induced Dissociation of Radical Cations". In his talk, he nicely showed the localization of double bond positions in lipids using collision-induced dissociation of radical cations generated by (+)APPI. Hereby, chlorobenzene has been used as a dopant in an LC-MS setup. This rule-based de-novo structural elucidation or library matching is a powerful tool for complex mixture analysis and enlarges the method toolbox for APPI-MS.

- **Ole Tiemann,** a PhD student from the University of Rostock (Rostock, Germany) from the group of Prof. Ralf Zimmermann, presented the "Detailed comparison of Xenon APPI (9.6/8.4 eV), Krypton APPI (10.6/10.0 eV), APCI, and APLI (266 nm) for gas chromatography high resolution mass spectrometry of standards and complex mixtures". He presented the utilization of a Xenon-filled discharge lamp for APPI and pointed out similarities and differences compared to the established Krypton-filled discharge lamp APPI sources as well as APCI (corona-needle) and APLI (Nd:YAG 4^{th} harmonic at 266 nm, 4.66 eV). Exemplarily, Xe-APPI and APLI offer the benefit

of not ionizing most impurities and column blood found in gas chromatography hyphenation, giving a clear background with low chemical noise, particularly useful for trace analysis or unknown search. His main proposition is to combine different photoionization schemes for complex mixture analysis.

As a conclusion, photoionization – with a strong focus on atmospheric pressure photoionization – offers a large variety of analytical capabilities in mass spectrometry. Method development, such as fragmentation on radical cations (rarely observed in ESI), involvement of ion chemistry and dopant reactions as well as adapting light sources (Xe-APPI, lasers), is far from finished and will become even more important facing new analytical challenges in environmental sciences, 'omics and energy transition. Ideally, data from multiple ionization schemes need to be combined for analysis of these complex molecular systems, which also involves established techniques, such as ESI and APCI.

The workshop started later due to a delay in a previous assembly meeting. Despite the low number of attendees, a good discussion was established, and the full timeframe has been used. Follow-up discussions in smaller groups have then continued even afterward. Next year's workshop will be organized by Lukas Hanley and Sven Ehlert (serving again as a volunteer from 2024).

Interest Group: Photoionization Mass Spectrometry

09 Workshop - What are the future needs of photoionization mass spectrometry for complex mixture analysis?

Presiding: Luke Hanley, Christopher P. Rüger

71st ASMS Conference on Mass Spectrometry and Allied Topics
June 4 - 8, 2023, Houston, Texas

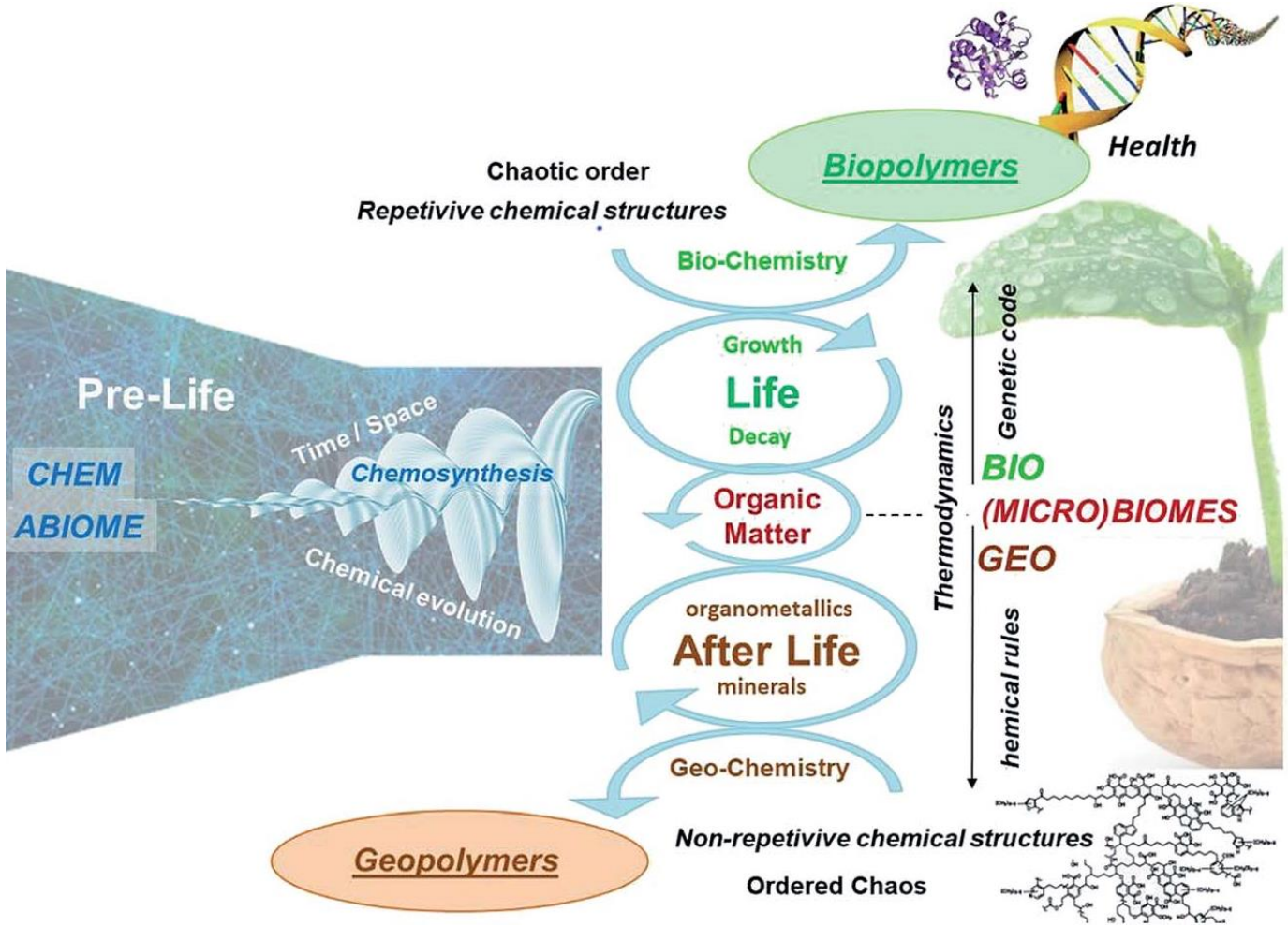
Workshop Lineup and Schedule

Prof. Janne Jänis
University of Eastern Finland
Joensuu, Finland

Patrick Müller
University of Geneva
Geneva, Switzerland

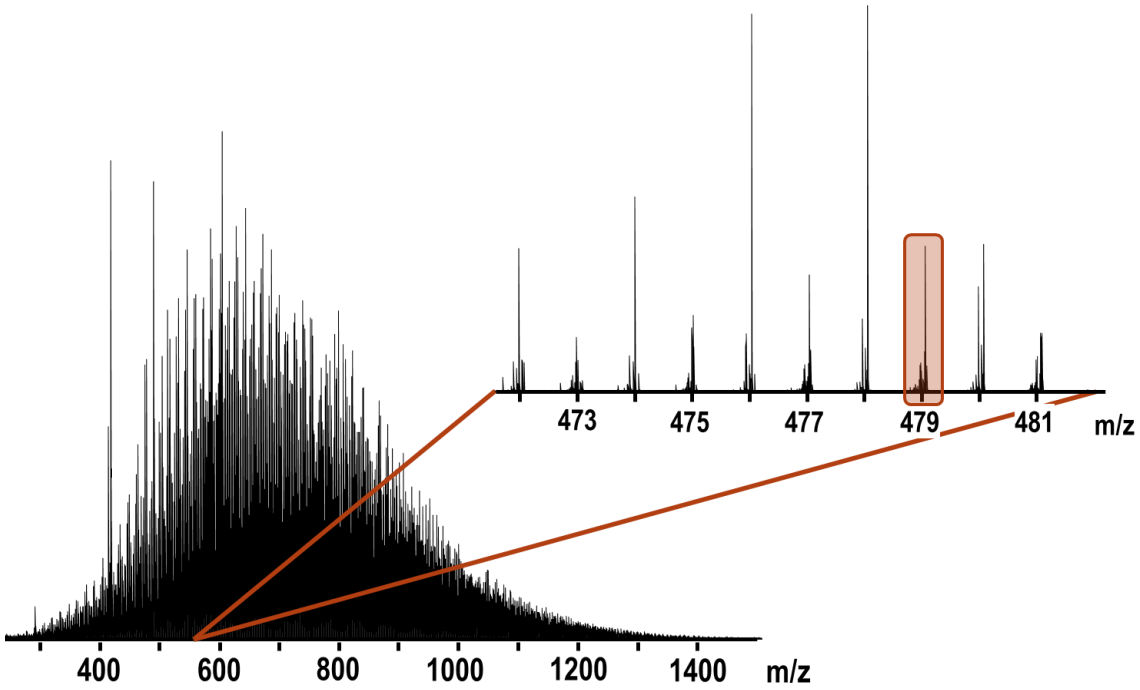
Ole Tiemann
University of Rostock
Rostock, Germany

What are Complex Mixtures?



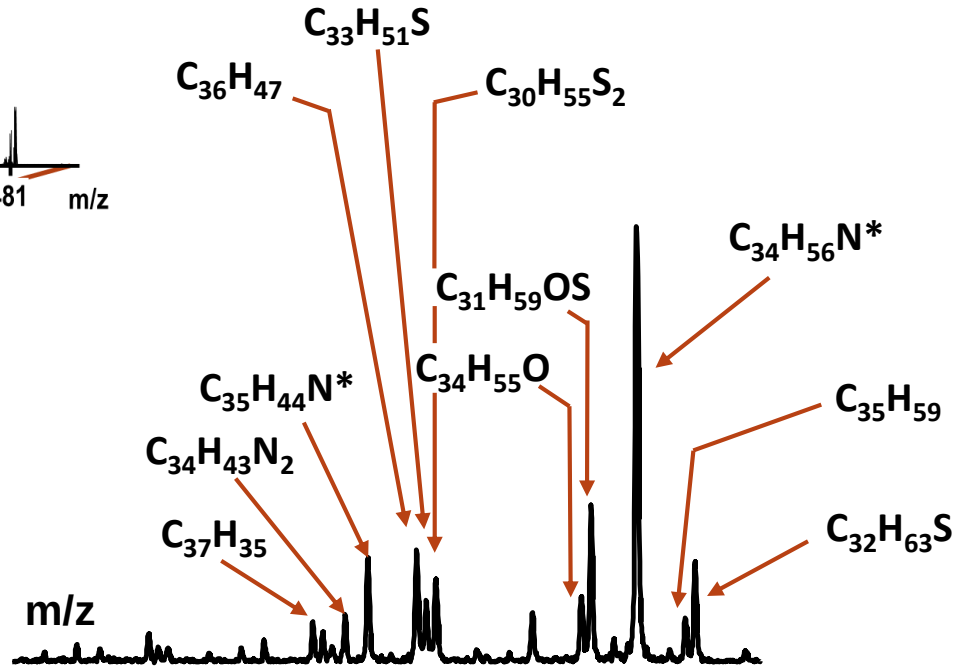
Schmitt-Kopplin et al., *Faraday Discussions*, **2019**, *218, 9-28*

Complex Mixture Mass Spectrometry

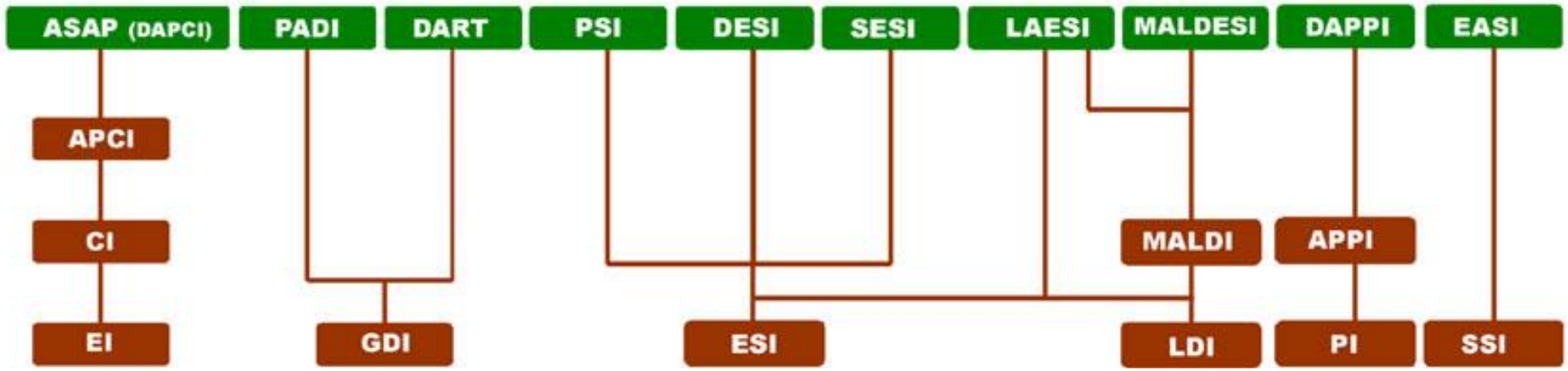


Every $C_cH_hN_nO_oS_s$ mass is unique!

Mass defect =
Atom mass – nearest integer mass



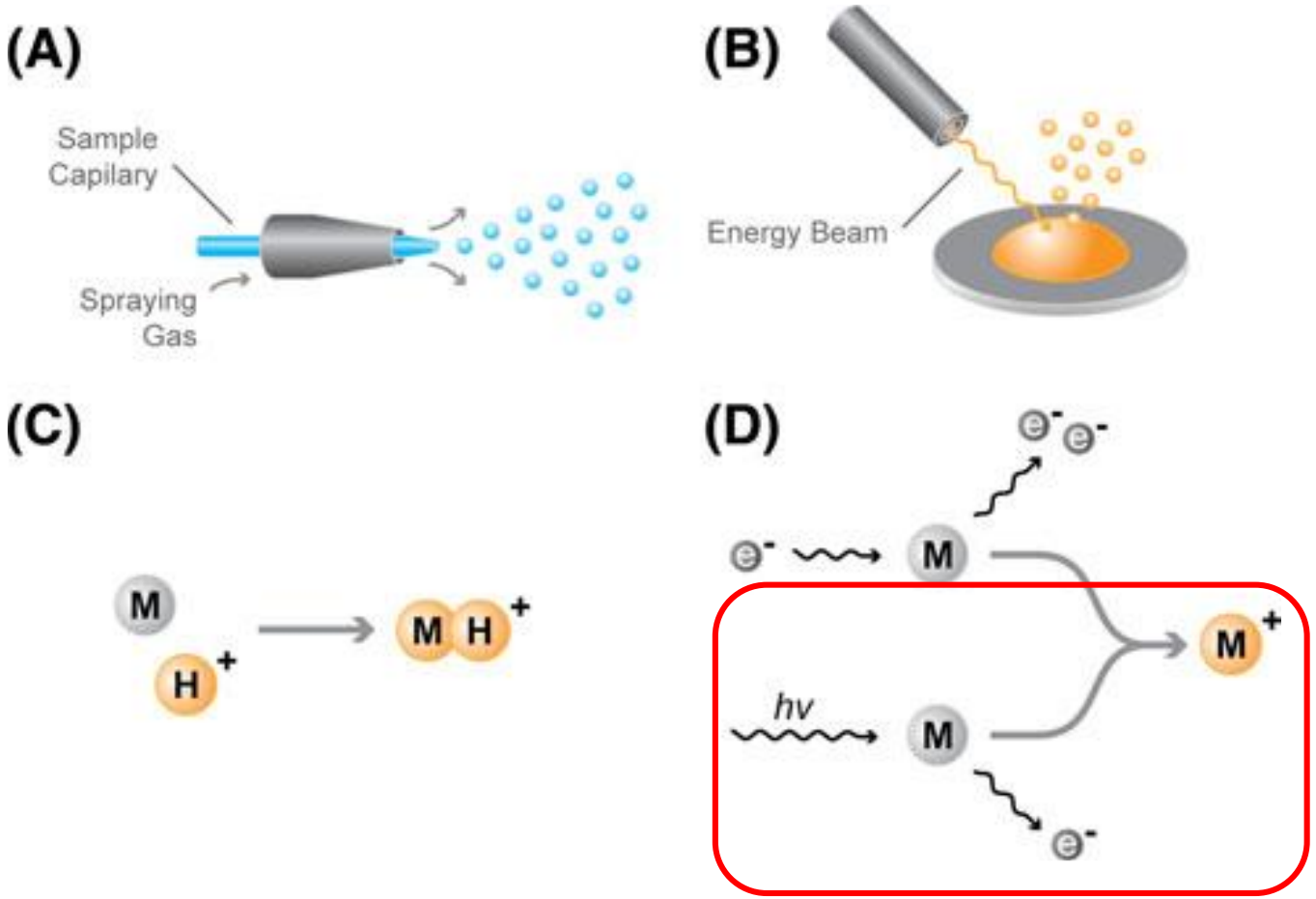
Creating Ions – Main Pathways



Simplified “ionization tree” – “root” technique given in brown and selected concepts based on them in green

Alberici et al., *Anal Bionanal Chem*, **2010**, 398:265–294

Basic Physical Concepts and Schemes for Ionization



A) Spray Ionization

B) Desorption Ionization

C) Chemical Ionization

D) Electron/Photon Ionization

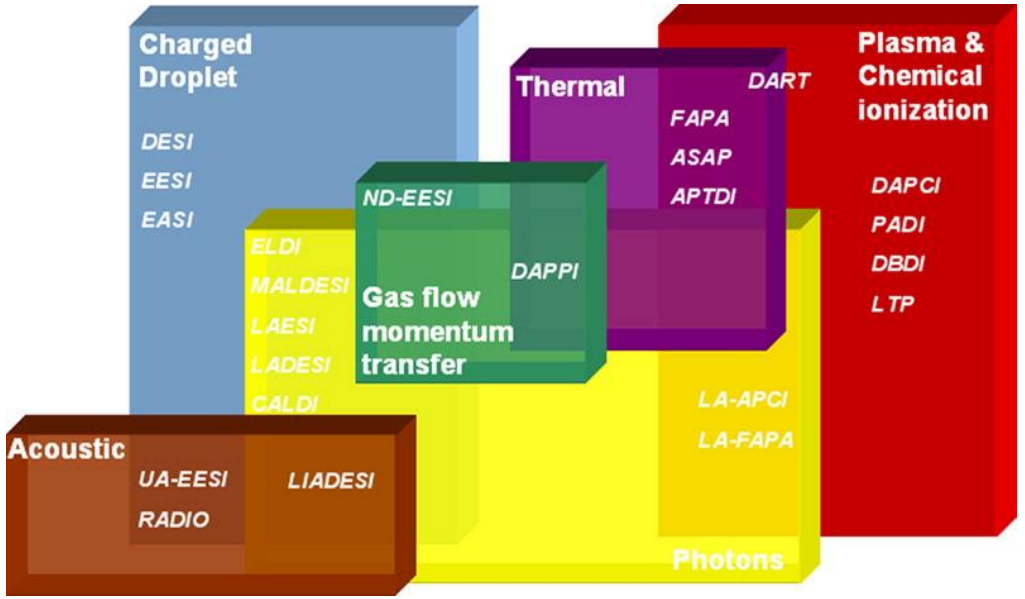
Pól et al., *Histochem Cell Biol*, **2010**, 134:423–443

Creating Ions – Main Physicochemical Pathways

Atomic Ionization	Molecular Ionization		
	Sample Phase	Mode	Pressure[a]
Thermal ionization	Gas phase	Electron ionization	HV
Spark source		Chemical ionization (CI)	IV
Glow discharge		Photoionization (PI)	HV
Inductively coupled plasma		Field ionization	HV
Resonance ionization		Metastable atom bombardment	HV
	Solution phase	Thermospray	LV
		Atmospheric-pressure CI	AP
		Atmospheric-pressure PI	AP
		Electrospray	AP
	Solid phase	Plasma desorption	HV
		Field desorption	HV
		Secondary-ion MS	HV
		Fast atom bombardment	HV
		Matrix-assisted laser desorption	HV

[a] HV, high vacuum; IV, intermediate vacuum; LV, low vacuum; AP, atmospheric pressure.

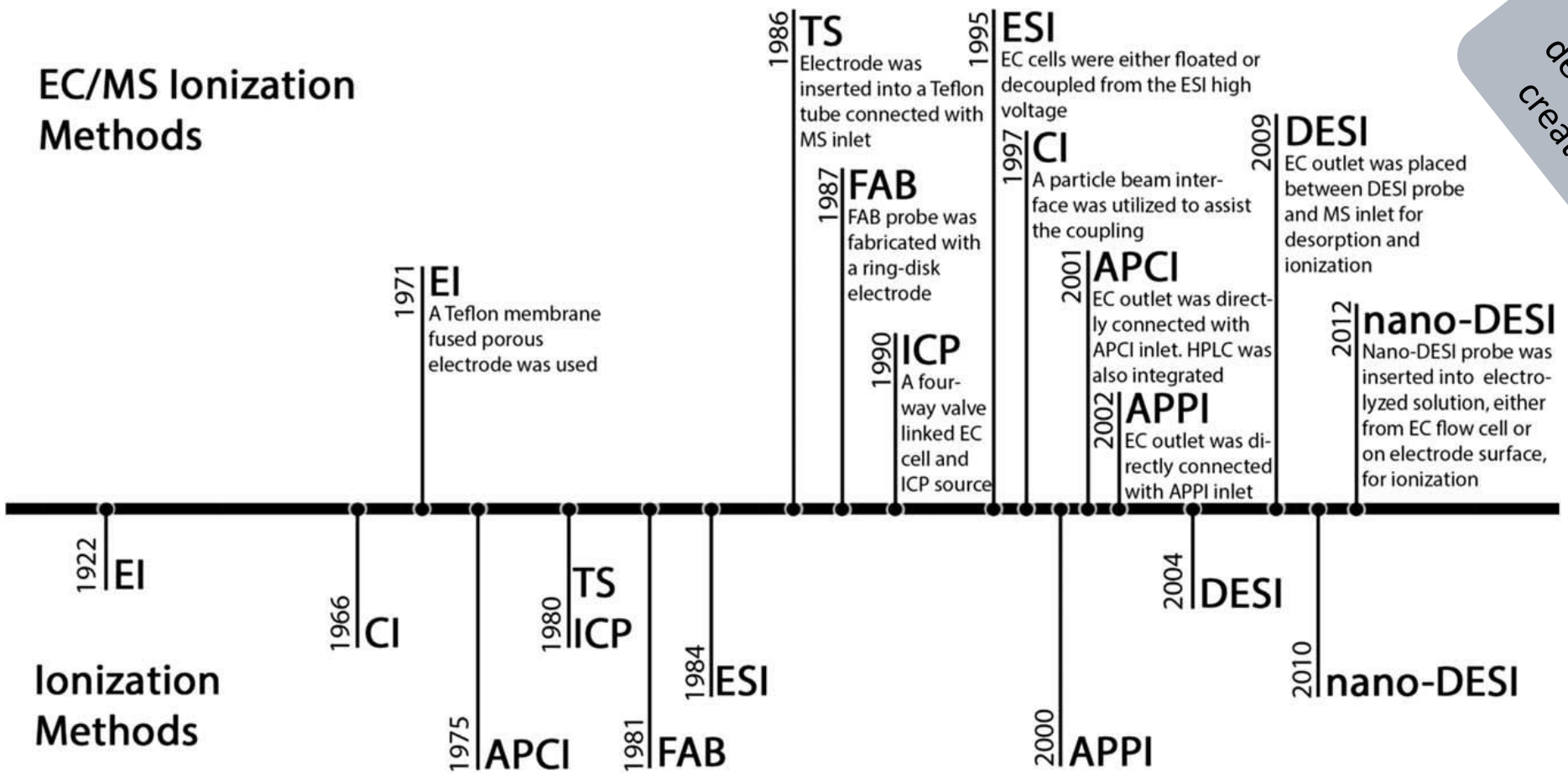
Jürgen H- Gross, *Mass Spectrometry – A Textbook*, **2017**, Spinger, ISBN *978-3-319-54398-7*



Structuring ionization concepts in MS with main physicochemical background

Chen et al., *JASMS*, **209**, 1947-1963

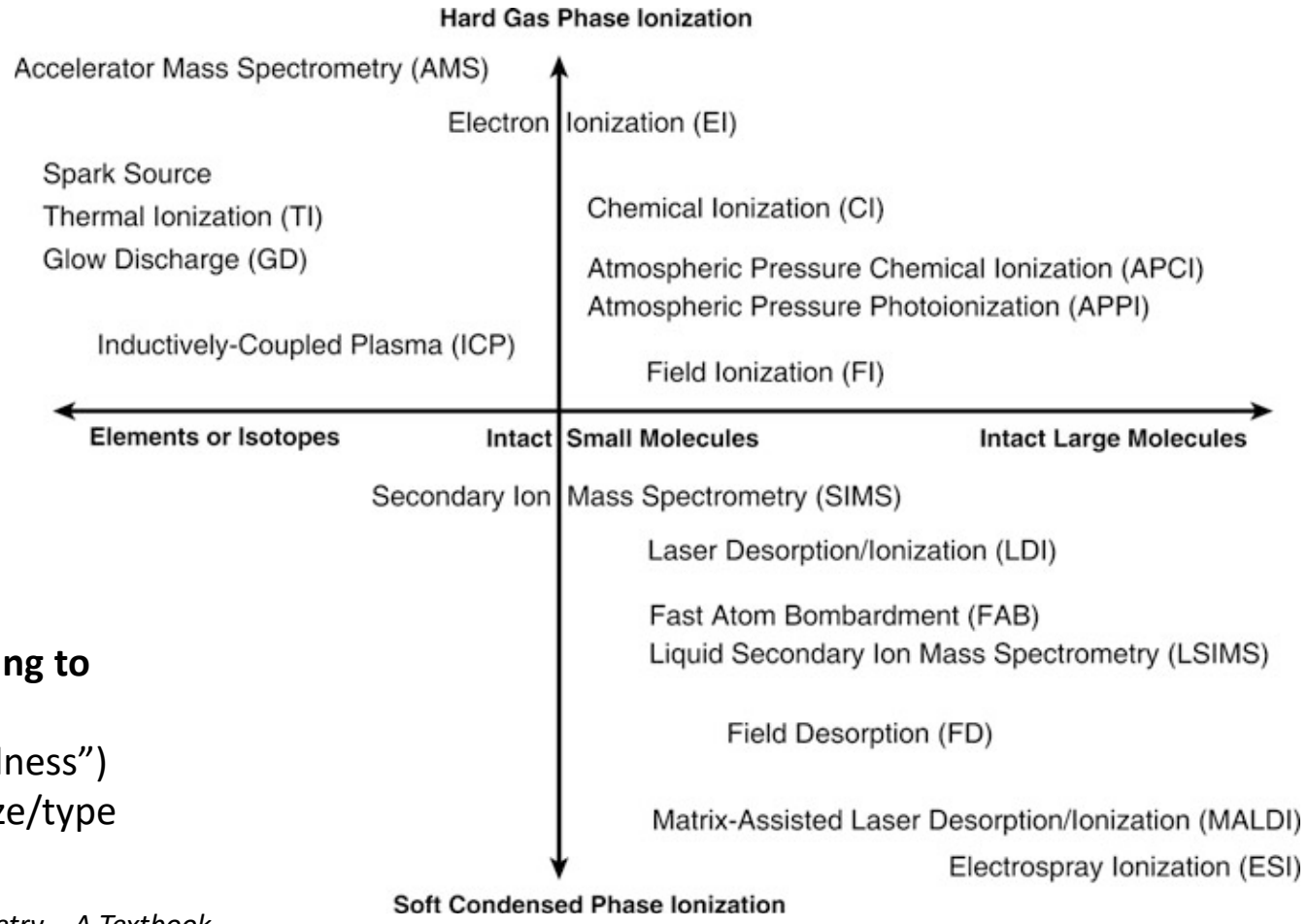
Timeline and the Ambient Ionization Techniques “Zoo”



After ~2013 endless variations of desorption and spray techniques creating an abbreviation „zoo“

Liu et al., *The Analyst*, **2013**, 138, 5519

Trying to get an overview of existing ionization concepts…



Structuring here according to

- energy uptake (“hardness”)
- molecular/analyte size/type

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Photoionization

Soft ionization of analytes by photon irradiation

at atmospheric pressure

Most often divided in:

- **a**tmospheric **p**ressure **p**hoto **i**onization utilizing rare gas discharge lamps (APPI using Krypton lamps, 10/10.6 eV)
- **a**tmospheric **p**ressure **l**aser **i**onization (APLI, most often 248/266 nm)

APPI

NdYag-Laser (266nm)
2 x 4,66eV = 9,3eV

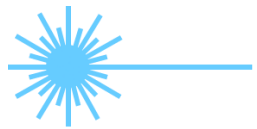
at reduced pressure / vacuum

Most often divided in:

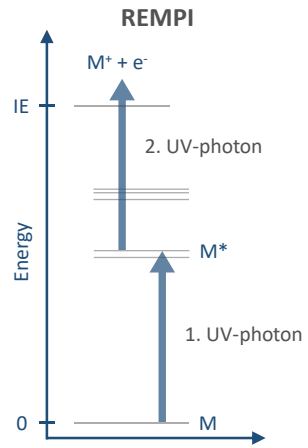
- **s**ingle-**p**hoton **i**onization (SPI) using VUV laser, synchrotron radiation or discharge lamps
- **r**esonance-**e**nhanced **m**ulti**p**hoton **i**onization (REMPI)

no matrix effects

almost no fragmentation



F2-Laser (157nm)
7.9eV



Workshop Lineup and Schedule

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University of Eastern Finland
Joensuu, Finland

What are the future needs of photoionization mass spectrometry for complex mixture analysis?

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Geneva, Switzerland

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