Charge Detection Mass Spectrometry Approaches for Ultra-High-Molecular-Weight Polymers: Playing with Heavier Things.

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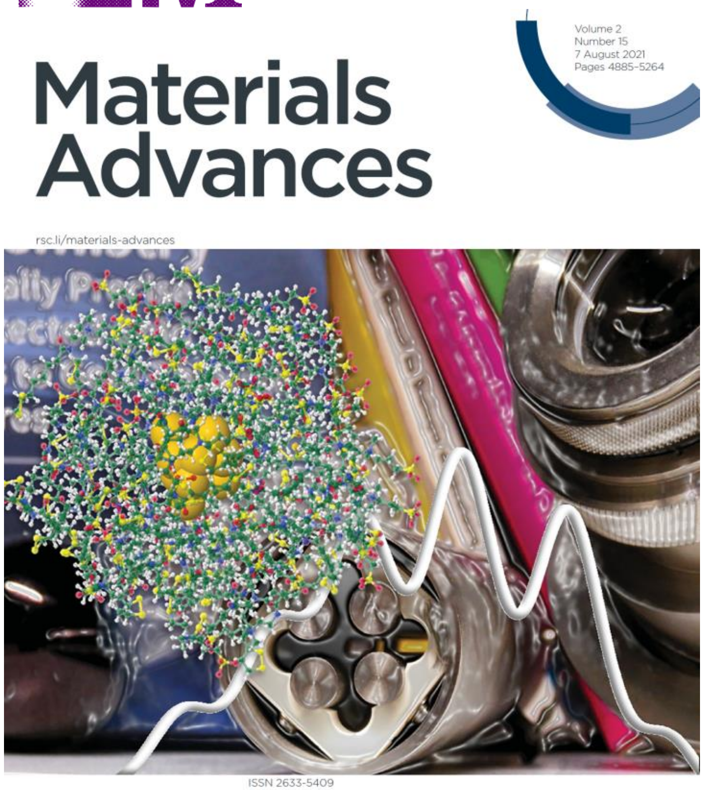
Fall 2021 virtual meeting of the ASMS Polymeric Materials Interest Group
2021, November 17th

iLM

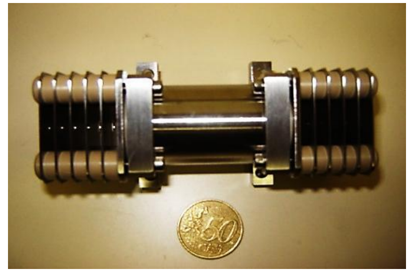


ROYAL SOCIETY OF CHEMISTRY

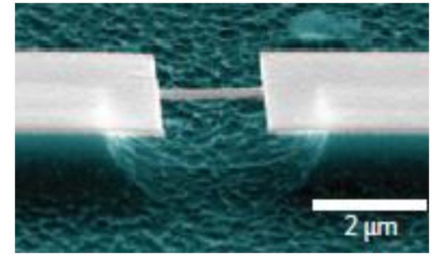
PERSPECTIVE
Rodolphe Antoine *et al.*
The emergence of mass spectrometry for characterizing nanomaterials. Atomically precise nanoclusters and beyond

Antoine et al
Mater. Adv., 2021, 2, 4896

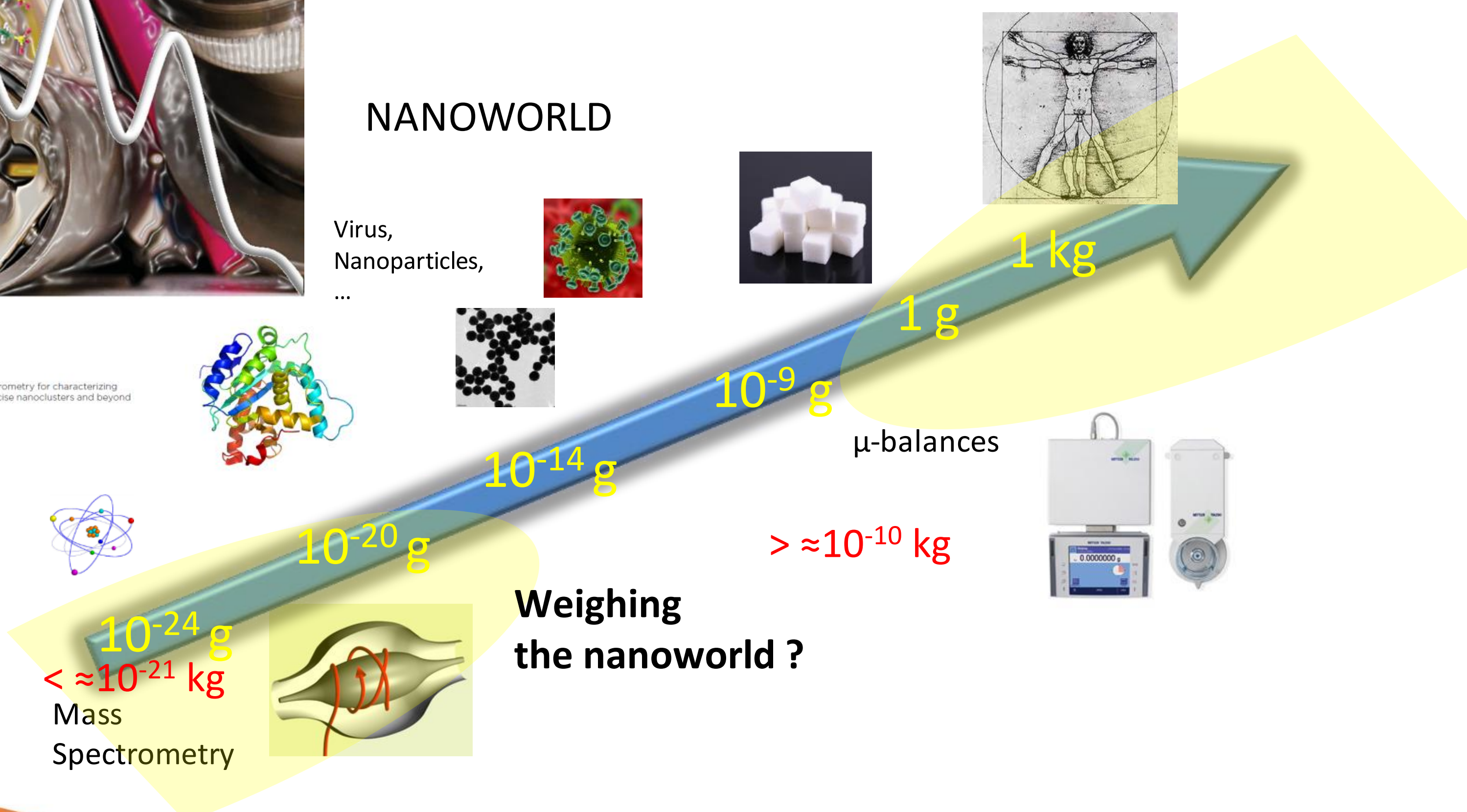
CHARGE-DETECTION MASS SPECTROMETRY



NEMS-MS



NANOWORLD



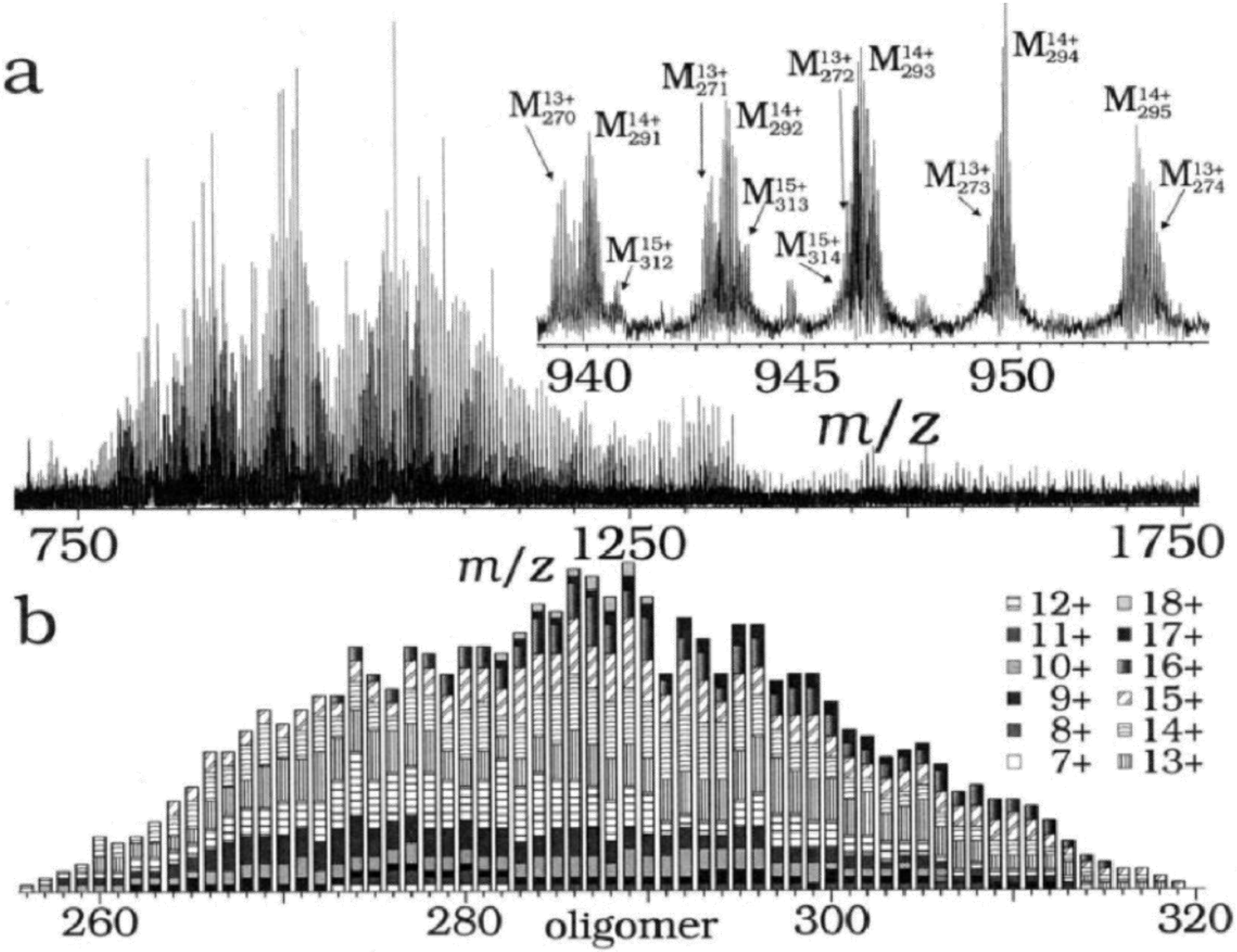
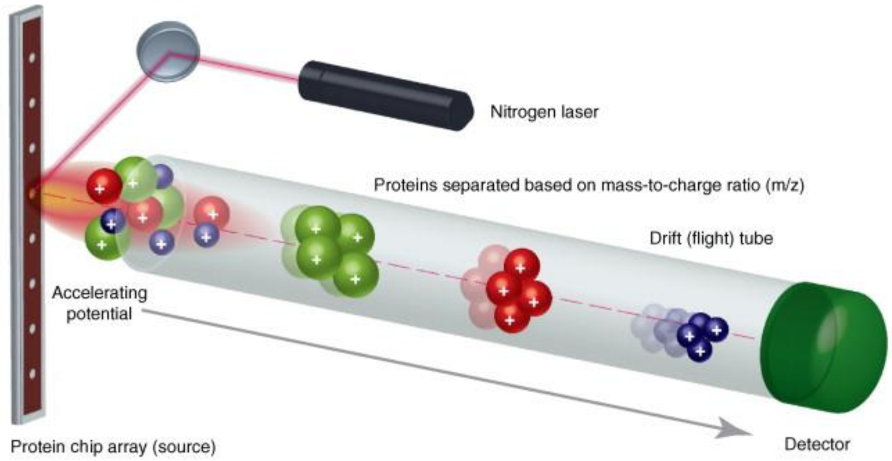


Figure 2. (a) ESI/FT mass spectrum of PEG 14000, RP = 10^5; (b) M_r distribution from summed oligomer abundances.

J. Am. Chem. Soc. **1995,** *117,* 12826–12831

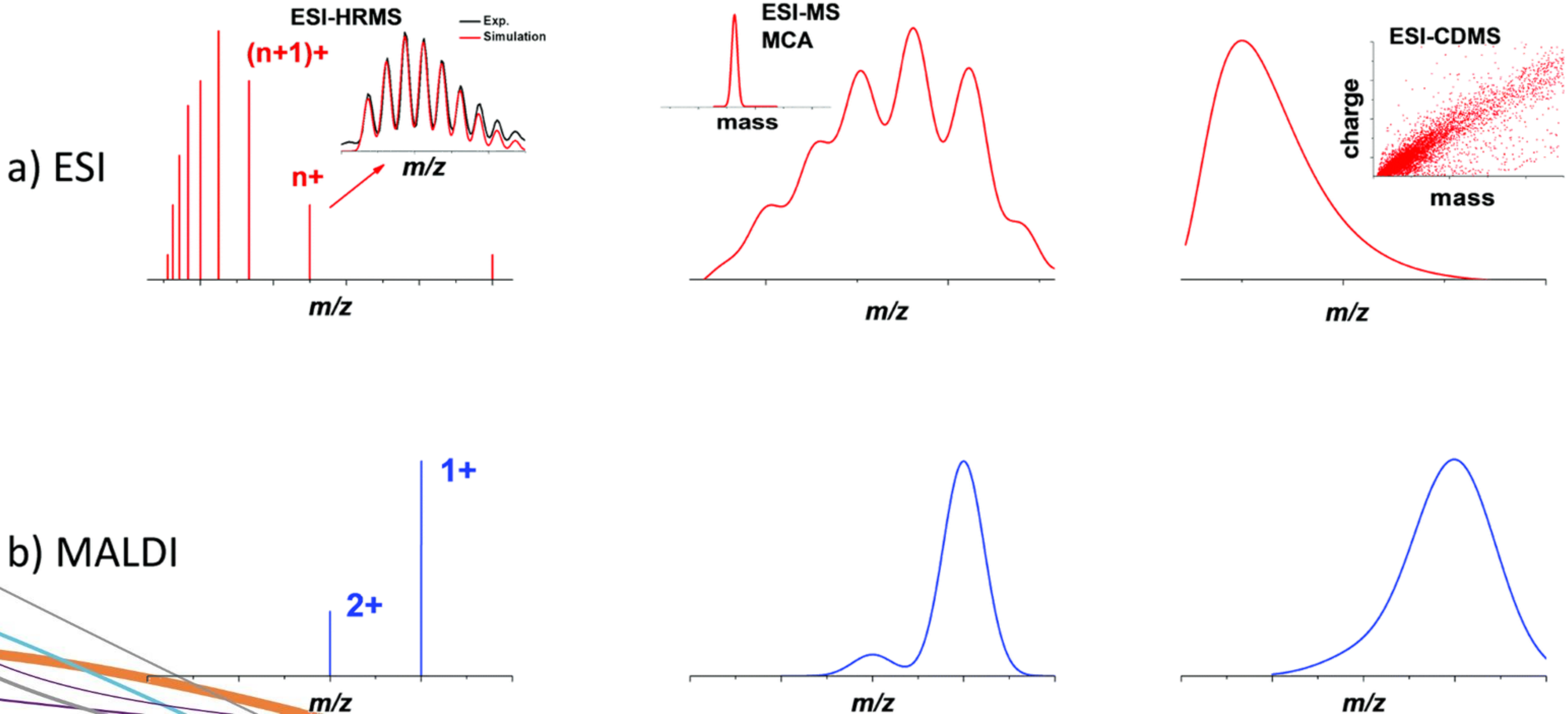
Oligomer Characterization of 4–23 kDa Polymers by Electrospray Fourier Transform Mass Spectrometry

Peter B. O'Connor and Fred W. McLafferty*



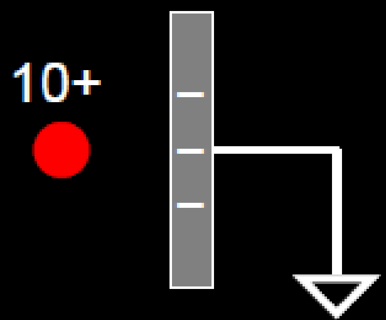
The mass-to-charge ratio of an ion is proportional to the square of its drift time.

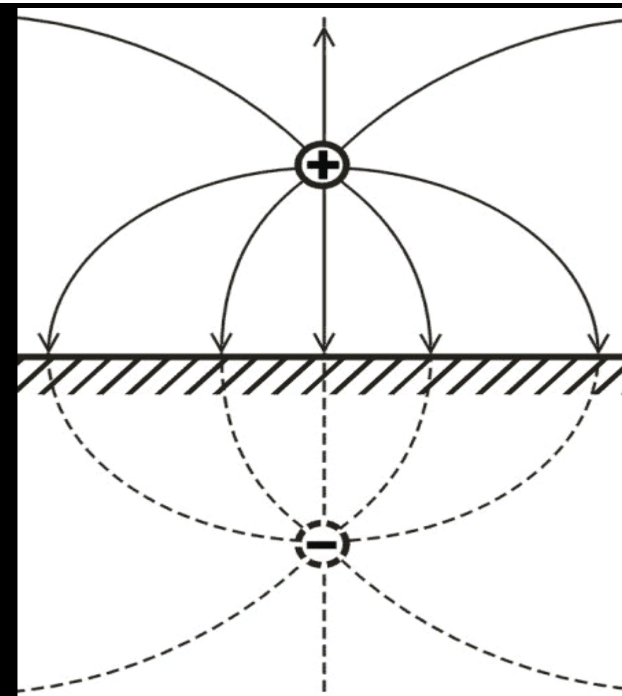
$$\frac{m}{z} = \frac{2t^2K}{L^2}$$

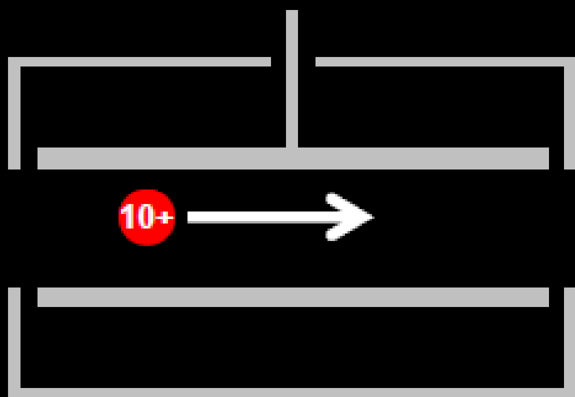


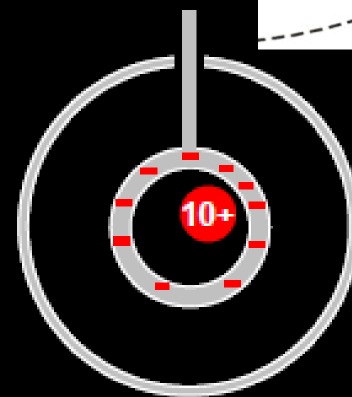
Charge detection mass spectrometry: How does it work ?

Image Charge Detection





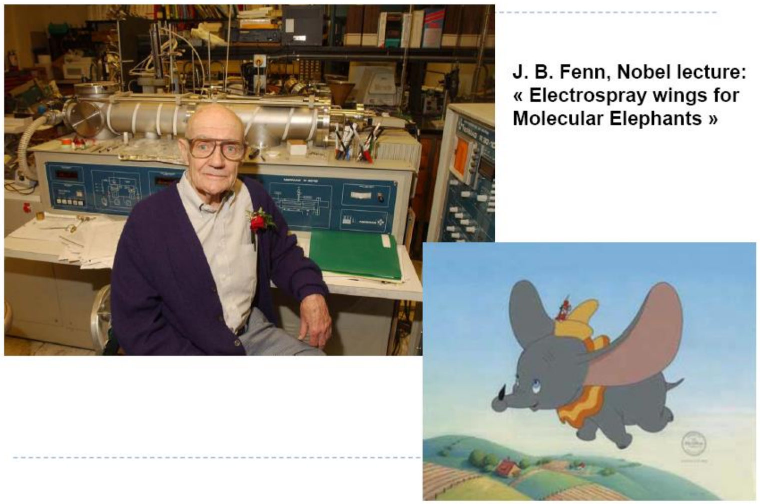




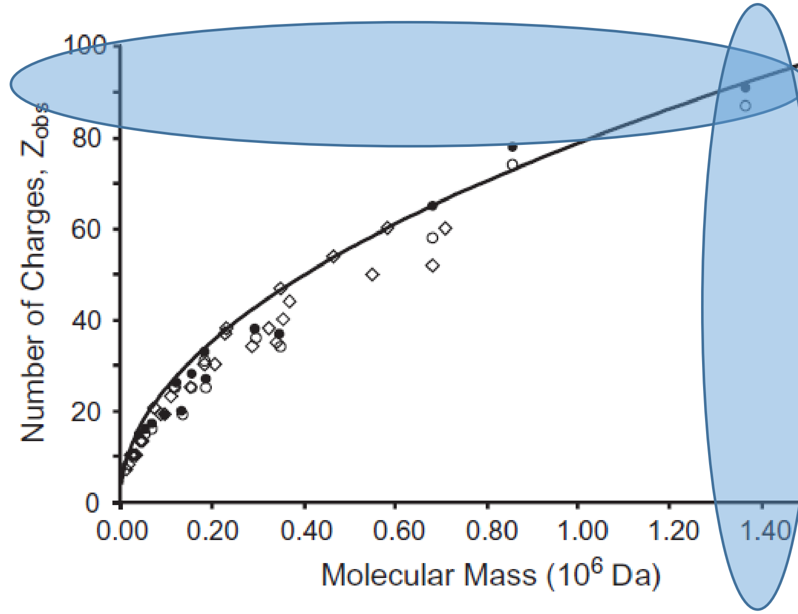
If the tube is long enough, the image charge = the charge on the ion

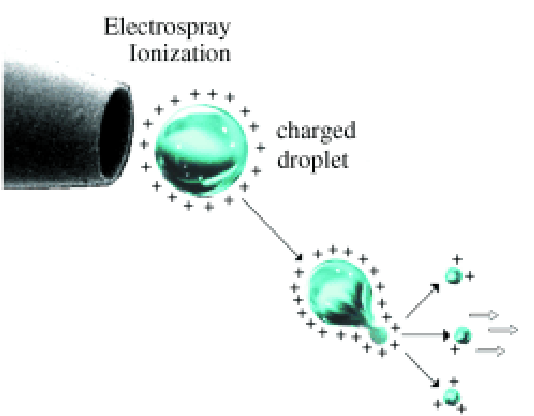
Electrospray and Image Charge-Detection
The perfect marriage for weighing heavier things !

Electrospray (ESI)



J. B. Fenn, Nobel lecture: « Electrospray wings for Molecular Elephants »





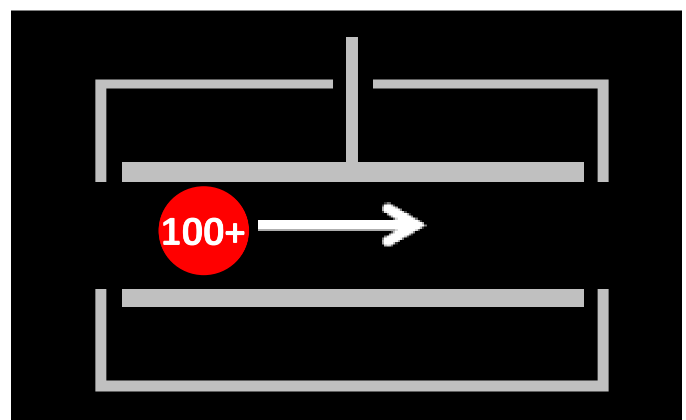
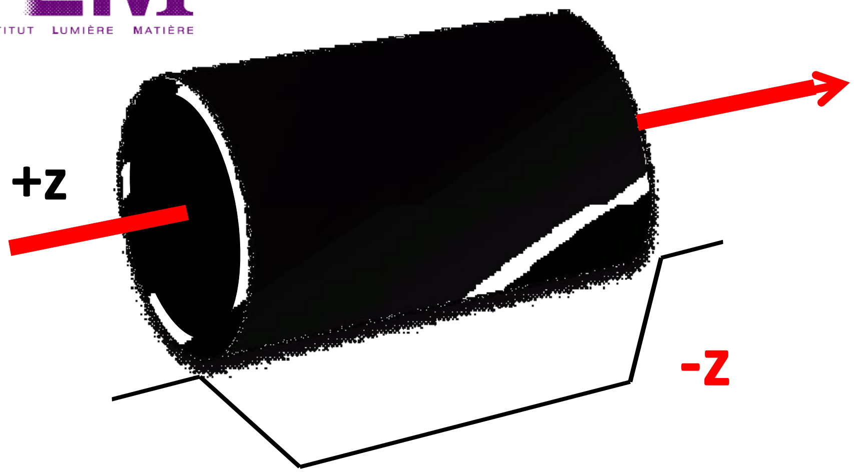


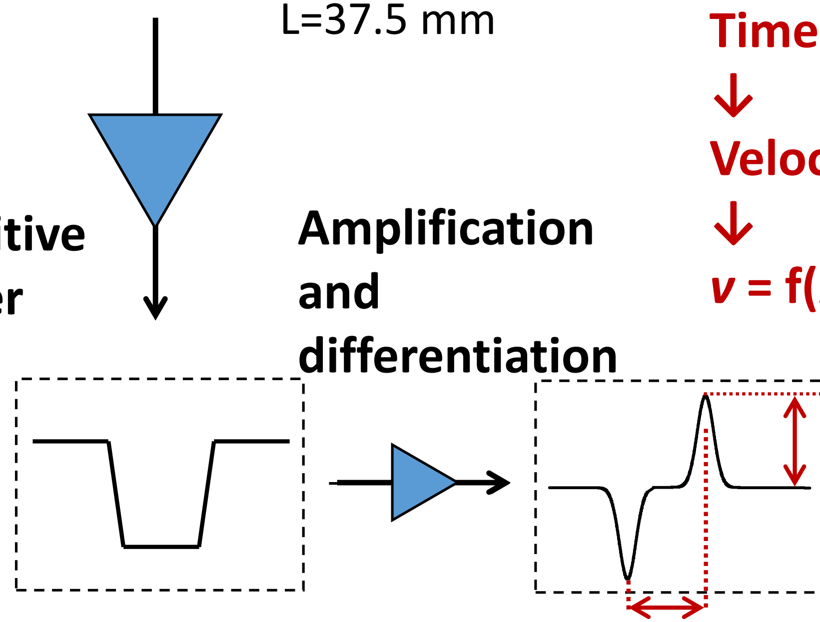
Image charge detection AND time-of-flight

Charge-Detection Mass Spectrometry



Charge (z) and velocity of the macroion are <u>simultaneously</u> recorded with the charge detector

L=37.5 mm



Low-noise charge sensitive pre-amplifier (JFET)

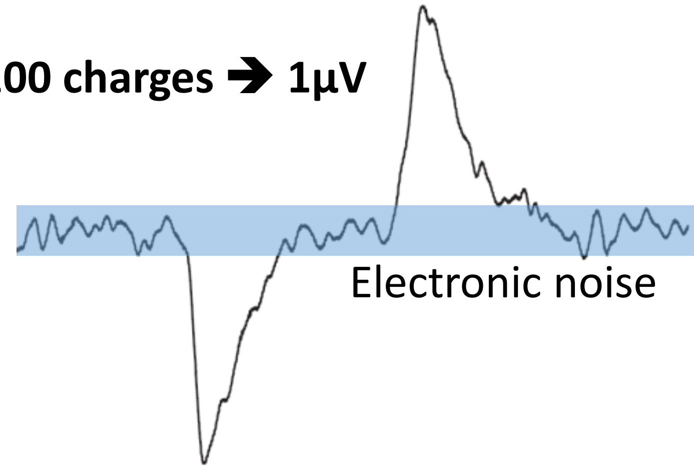
Amplification and differentiation

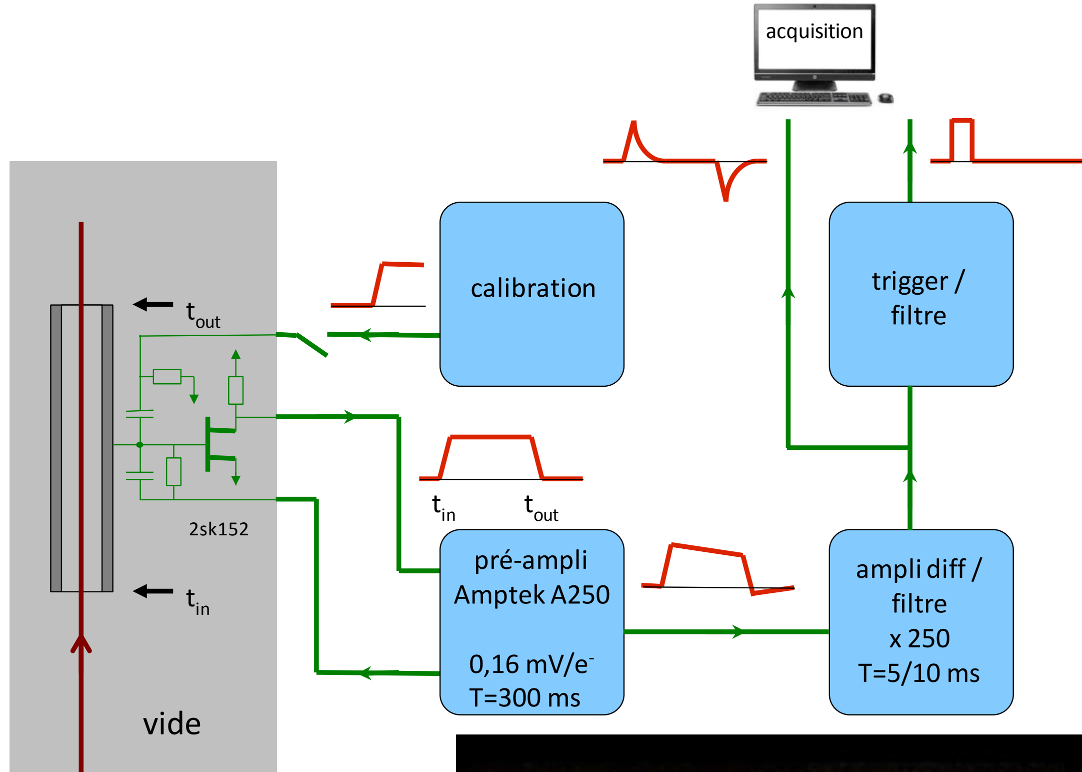
Time-of-Flight (*ToF*)
↓
Velocity *v*
↓
***v* = f(*m*/*z*)**

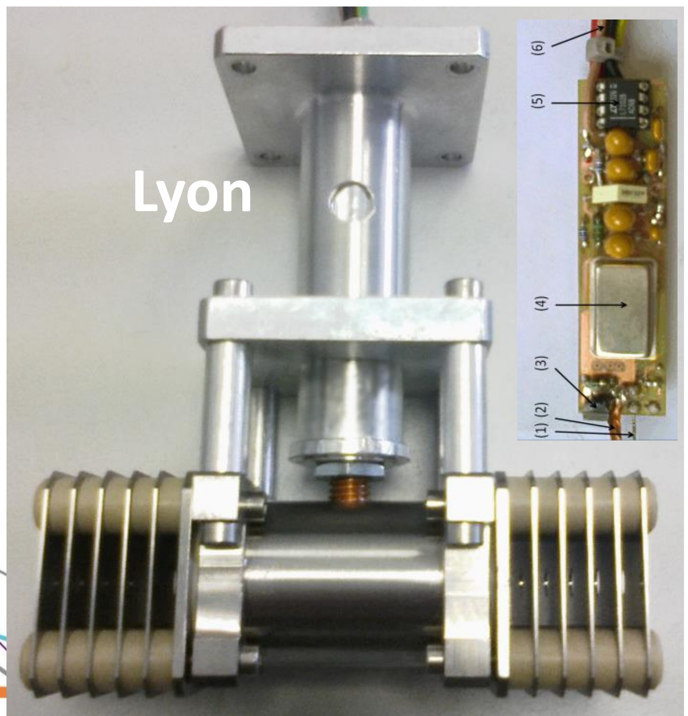
Z* ➔ *V*=*Ze*/*C

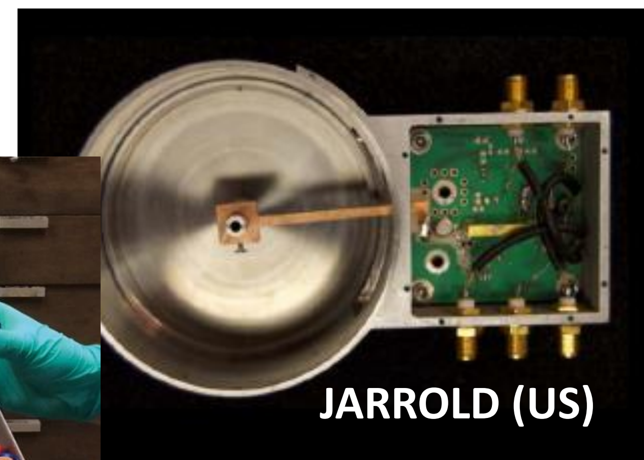
Doussineau T., RA, et al., *Rapid Commun. Mass Spectrom*. 2011, 25, 617

100 charges → 1µV







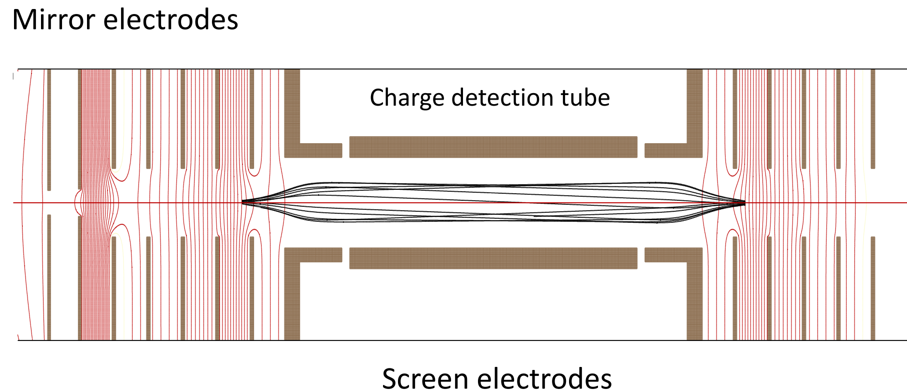


Volume 34, Issue S2
Special Issue: Polymer Mass Spectrometry
August 2020
e8539

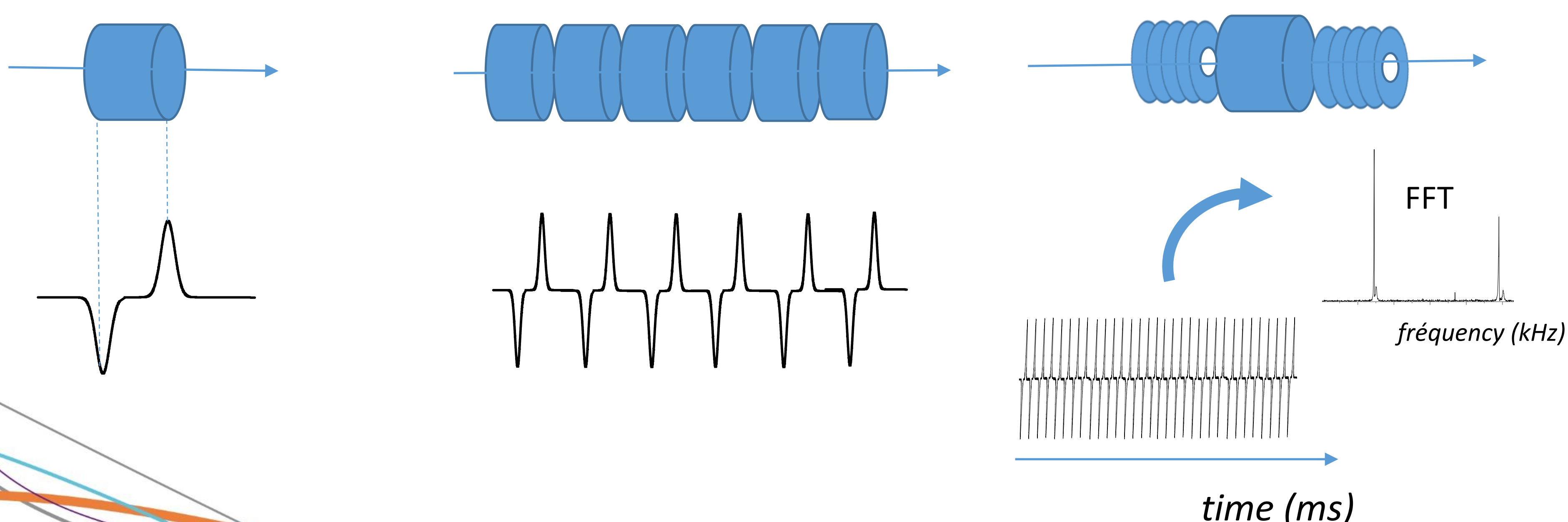
SPECIAL ISSUE PERSPECTIVE

Weighing synthetic polymers of ultra-high molar mass and polymeric nanomaterials: What can we learn from charge detection mass spectrometry?

Rodolphe Antoine

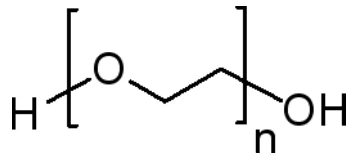


Single pass CDMS   linear array CDMS   ion trap CDMS

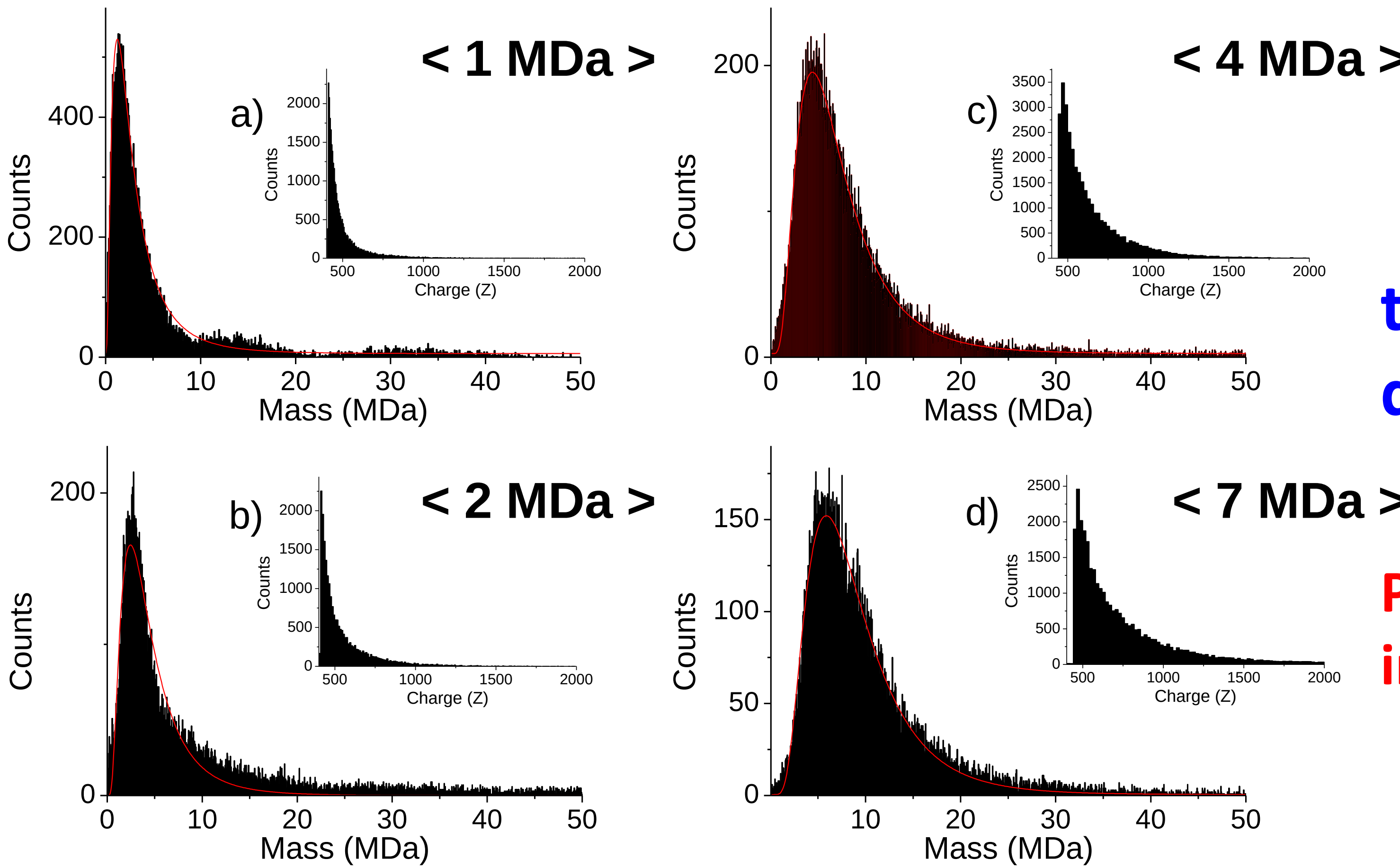


CDMS mode	Ion count rate(ions/s)	Charge uncertainty (e)	Limit of détection (e)	Mass resolution	Working mass window(Da)
CDMS – single pass	1000	50	200-250	5-7	10^{6}-10^{13}
CDMS-array	100	10	100	~10	10^{5}-10^{12}
CDMS-Ion trap	1 (400 ms trapping)	0,65	7	10-100	10^{4}-10^{8}

Charge detection mass spectrometry: What do we learn?



Poly(ethylene oxide)
POLYMER



true mass distribution

Polydispersity index

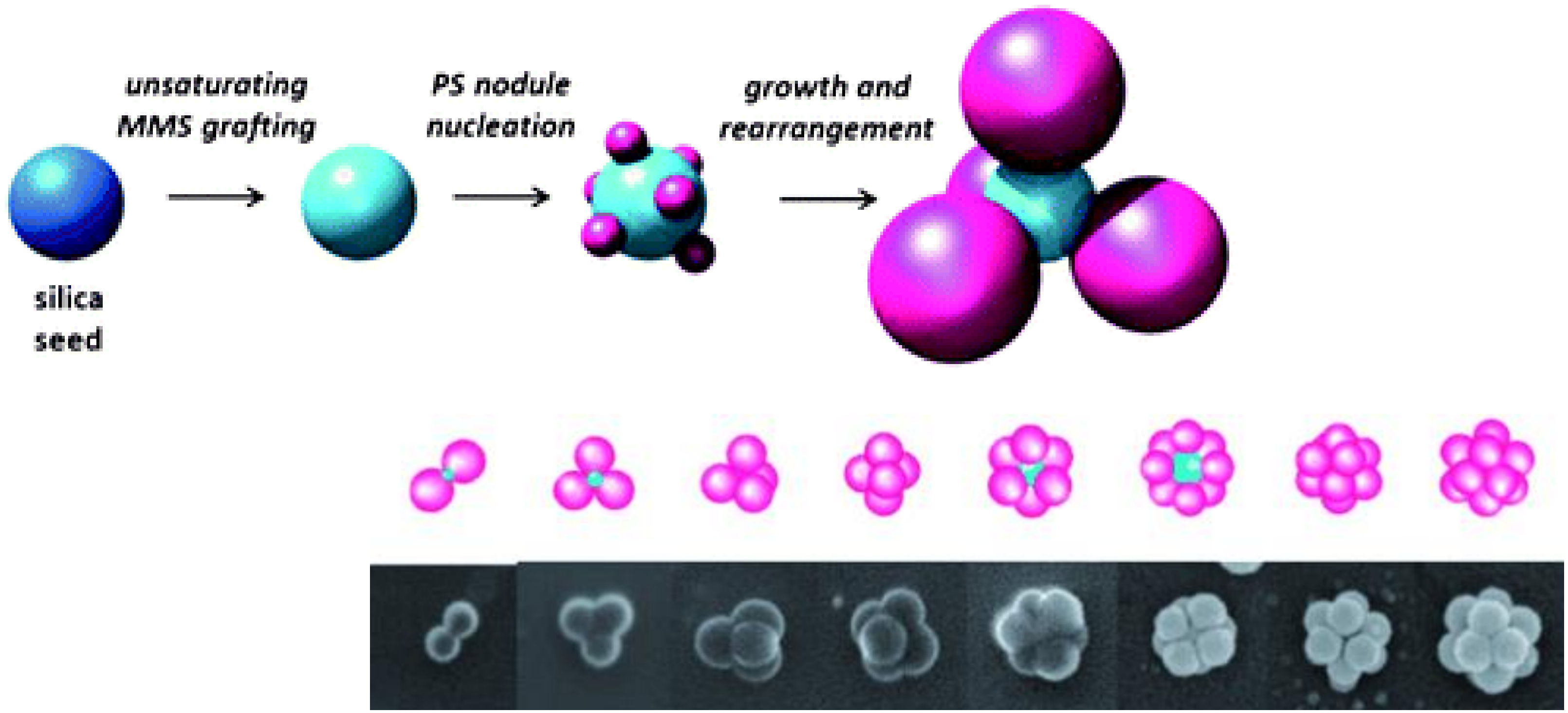
Respective mass distributions (and charges in inset) are histogrammed. They exhibit maxima at 1.4, 2.7, 4.4 and 6.2 MDa, respectively, as well as a high-mass tail.
The fit of MWDs leads to polydispersity index (I_p) values of 1.4, 1.6, 1.5 and 2.1,

Doussineau T., RA, et al., *Rapid Commun. Mass Spectrom.* 2011, 25, 617

PS-silica colloidal molecules obtained by latex surface nucleation and growth on silica seeds

Serge Ravaine and Etienne Duguet
CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac,

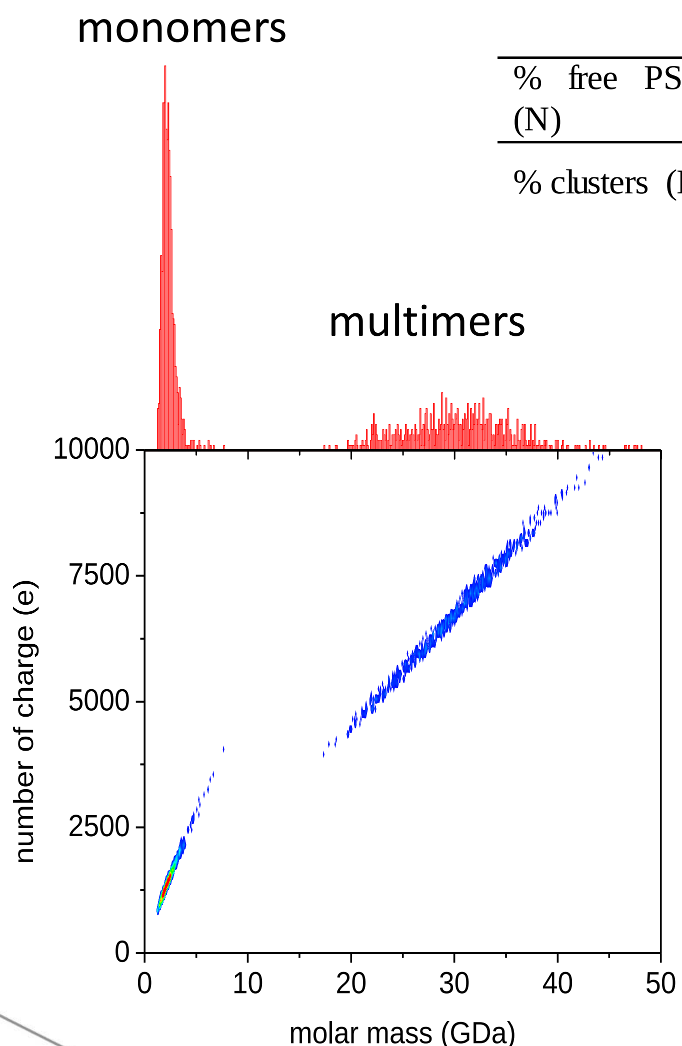
Muriel Lansalot and Elodie Bourgeat-Lami
Université de Lyon, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2)

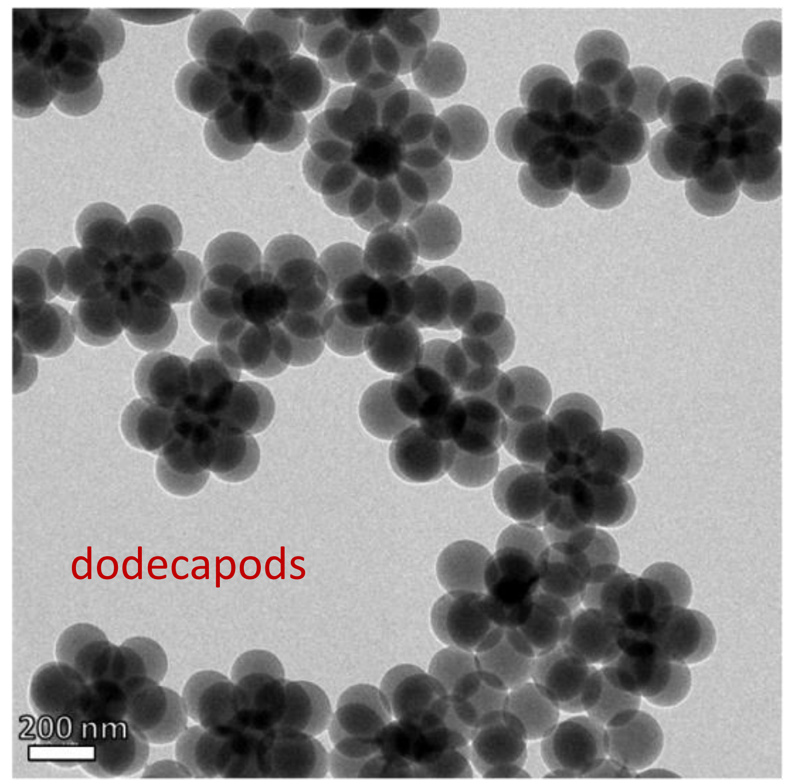


Ravaine et al. Angew. Chem., Int. Ed., 2009, 48, 361 ; Polym. Chem., 2012, 3, 1130

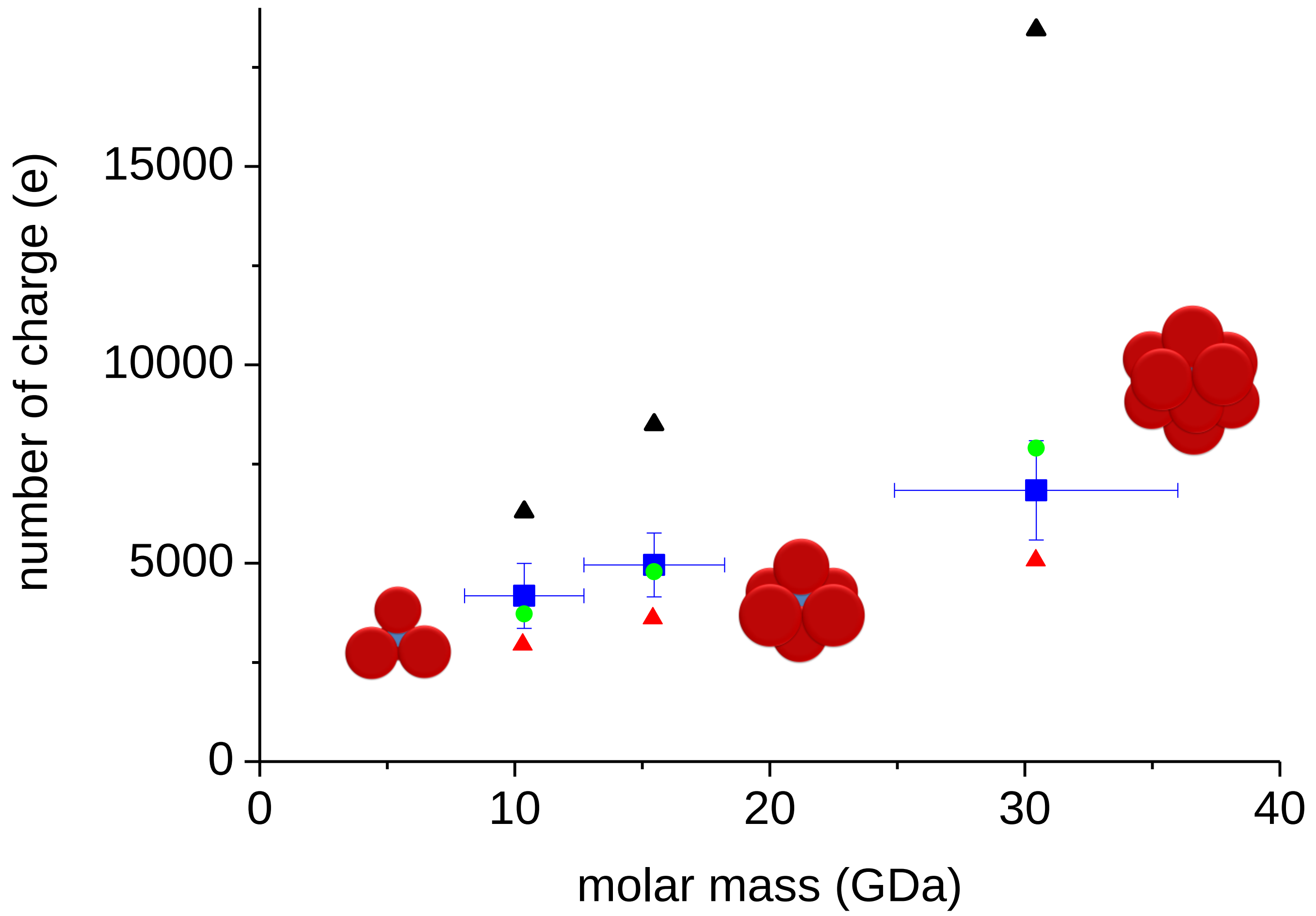
ESI-CDMS : An efficient complementary tool for NP characterisation

		tetrapods	hexapods	dodecapods
% free PS beads (N)	TEM	10.7 (140)	56.0 (659)	43.4 (319)
	ESI-CDMS	8.5 (146)	35.8 (846)	54.0 (836)
% clusters (N)	TEM	89.3 (1163)	44.0 (517)	56.6 (416)
	ESI-CDMS	91.5 (1564)	64.2 (1519)	46.0 (711)

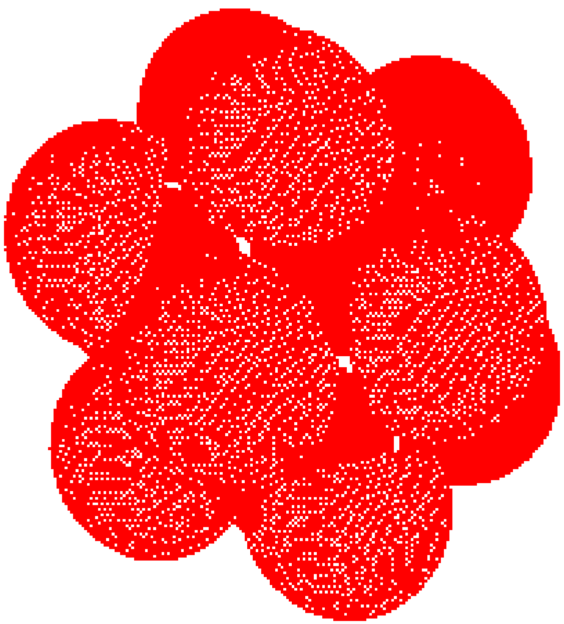


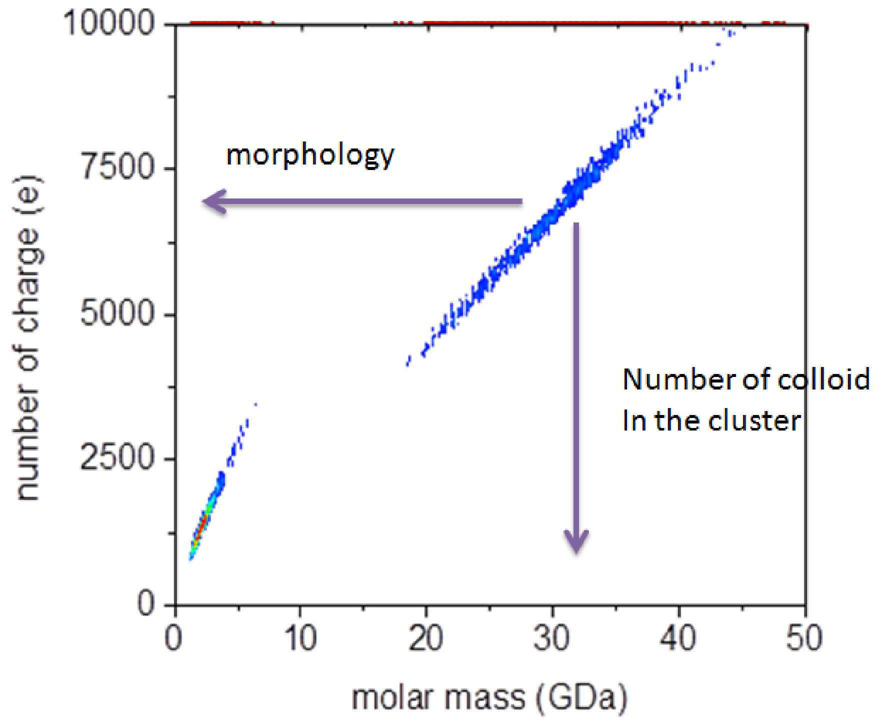


ESI-CDMS : An efficient complementary tool for NP characterisation



ESI-CDMS : An efficient complementary tool for NP characterisation





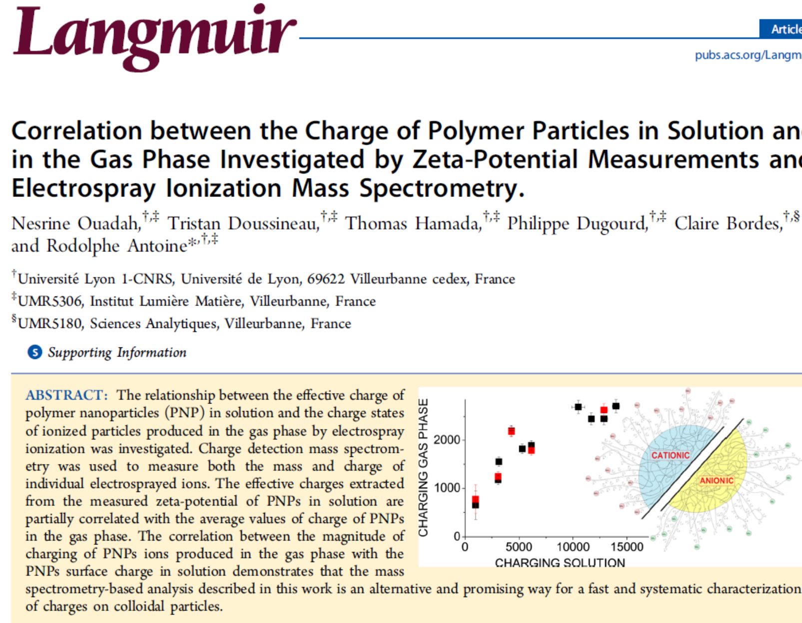
Doussineau, RA, et al.

The Journal of Physical Chemistry C **119**, 10844-10849 (2015)

Journal of the American Chemical Society **2015** *137* (5), 1929-1937

CDMS,

a kind of zetameter ?


Langmuir
Article
pubs.acs.org/Langmuir

Correlation between the Charge of Polymer Particles in Solution and in the Gas Phase Investigated by Zeta-Potential Measurements and Electrospray Ionization Mass Spectrometry.

Nesrine Ouadah,[†,‡] Tristan Doussineau,[†,‡] Thomas Hamada,[†,‡] Philippe Dugourd,[†,‡] Claire Bordes,[†,§] and Rodolphe Antoine*[,†,‡]

[†]Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France
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Supporting Information

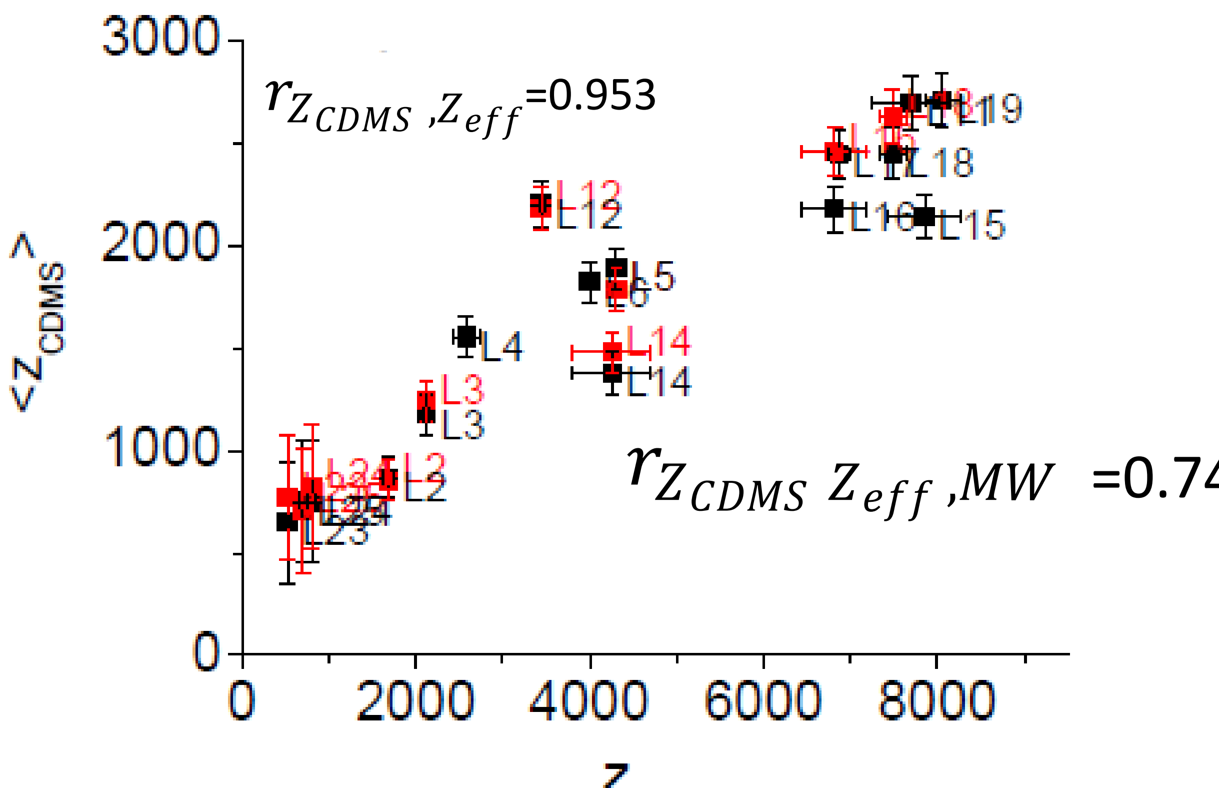
ABSTRACT: The relationship between the effective charge of polymer nanoparticles (PNP) in solution and the charge states of ionized particles produced in the gas phase by electrospray ionization was investigated. Charge detection mass spectrometry was used to measure both the mass and charge of individual electrosprayed ions. The effective charges extracted from the measured zeta-potential of PNPs in solution are partially correlated with the average values of charge of PNPs in the gas phase. The correlation between the magnitude of charging of PNPs ions produced in the gas phase with the PNPs surface charge in solution demonstrates that the mass spectrometry-based analysis described in this work is an alternative and promising way for a fast and systematic characterization of charges on colloidal particles.

Dynamic light scattering (DLS)
& Zetametry

➔ **Electrophoretic mobility (μ_{ep})**

Malvern®, Zetasizer NanoZS

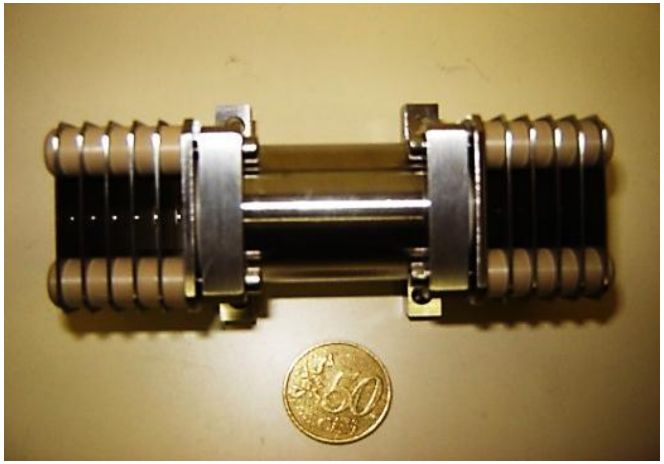
ZETA-POTENTIAL ζ



Charge-detection Mass spectrometry,

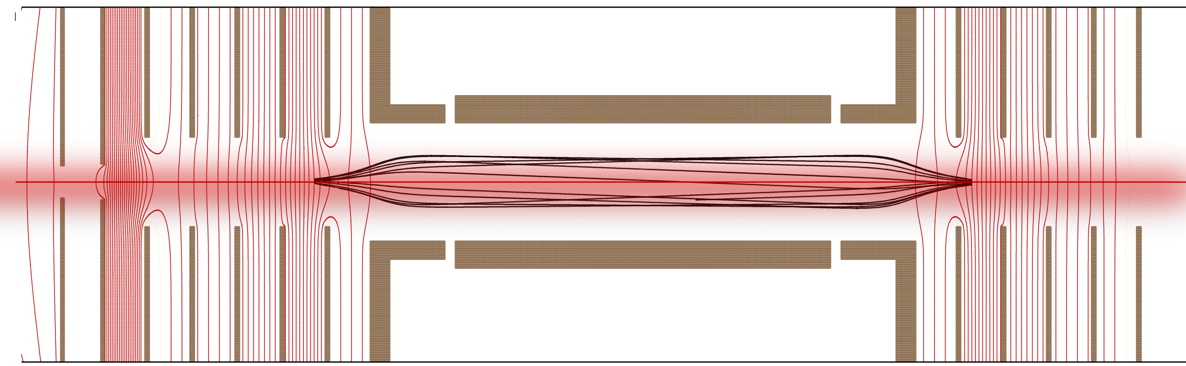
and couplings

Separative techniques

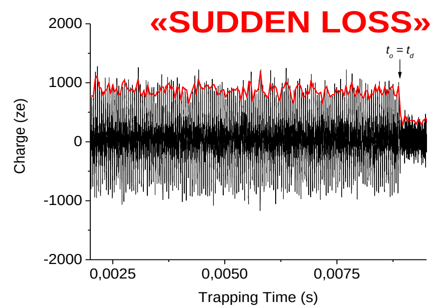


Photodissociation techniques

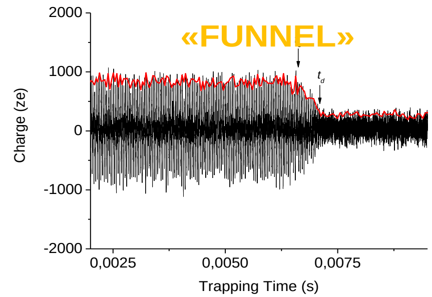
photofragmentation at the single molecule approach



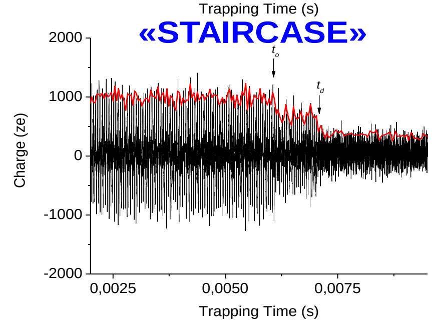
High power
CO_2 lasers (SYNRAD 25 W)



Fragment lost
Or low-charge fragments
(z<400 e)



(bio)polymer « peeling »
EVAPORATION

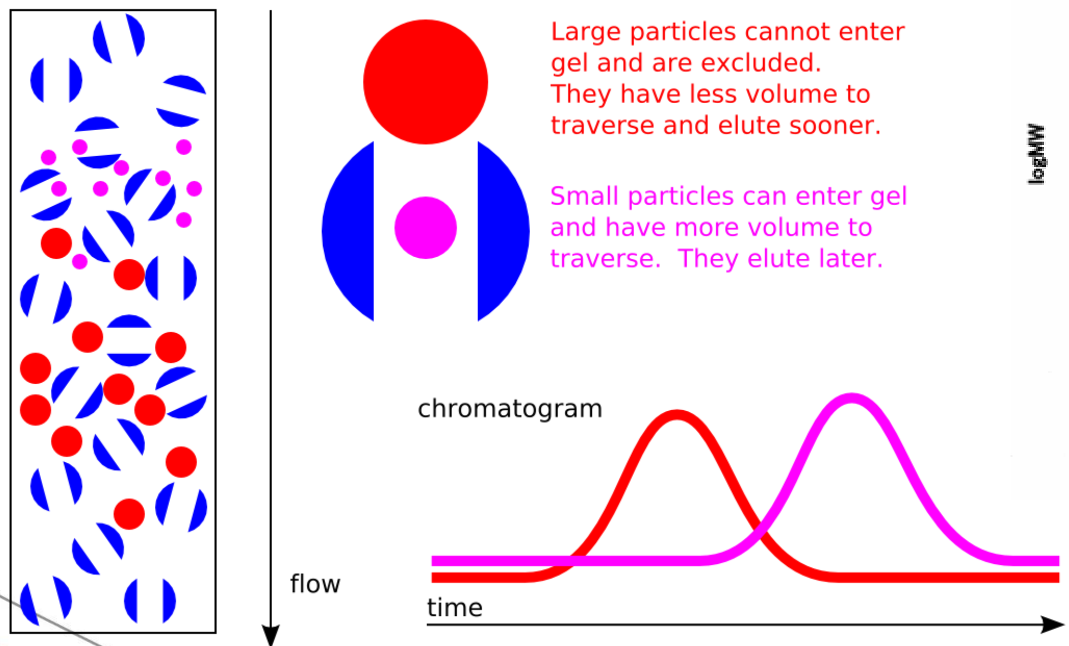


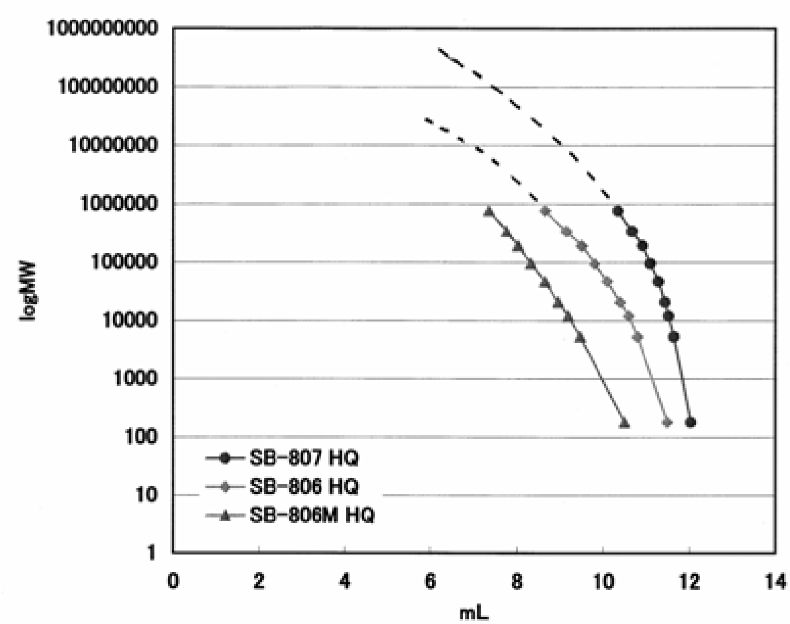
(asymmetric)
FISSION

Size-exclusion chromatography

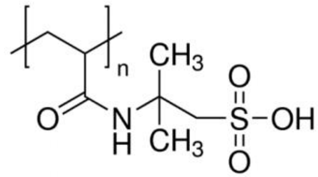
A chromatographic method in which molecules in solution are separated by their size

SHODEX column
807 et 806M HQ

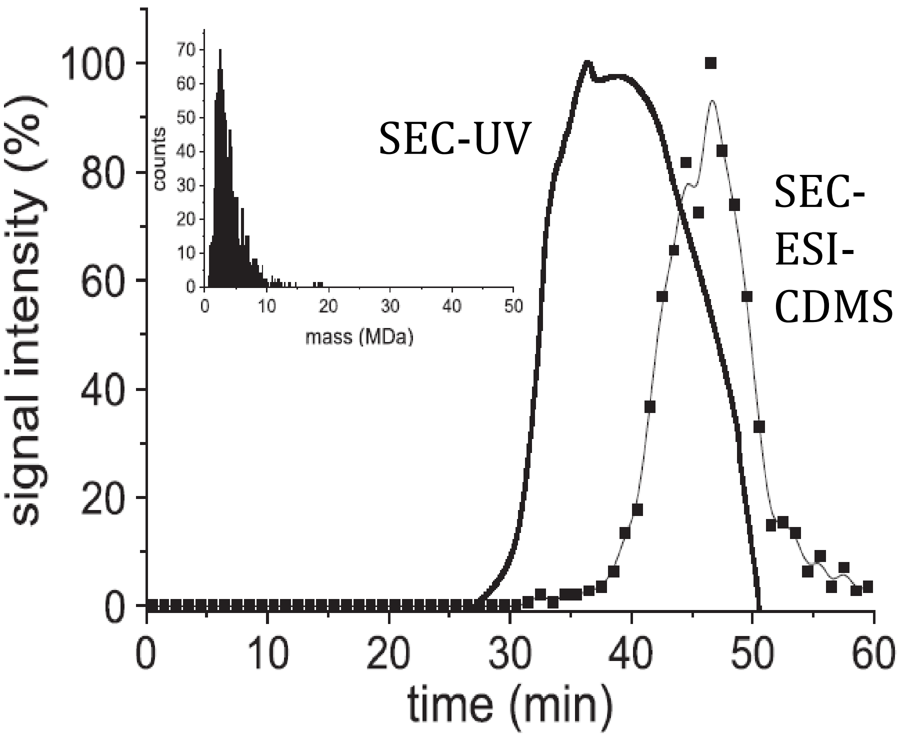




poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS 2MDa)



- SEC-UV & SEC-ESI-CDMS



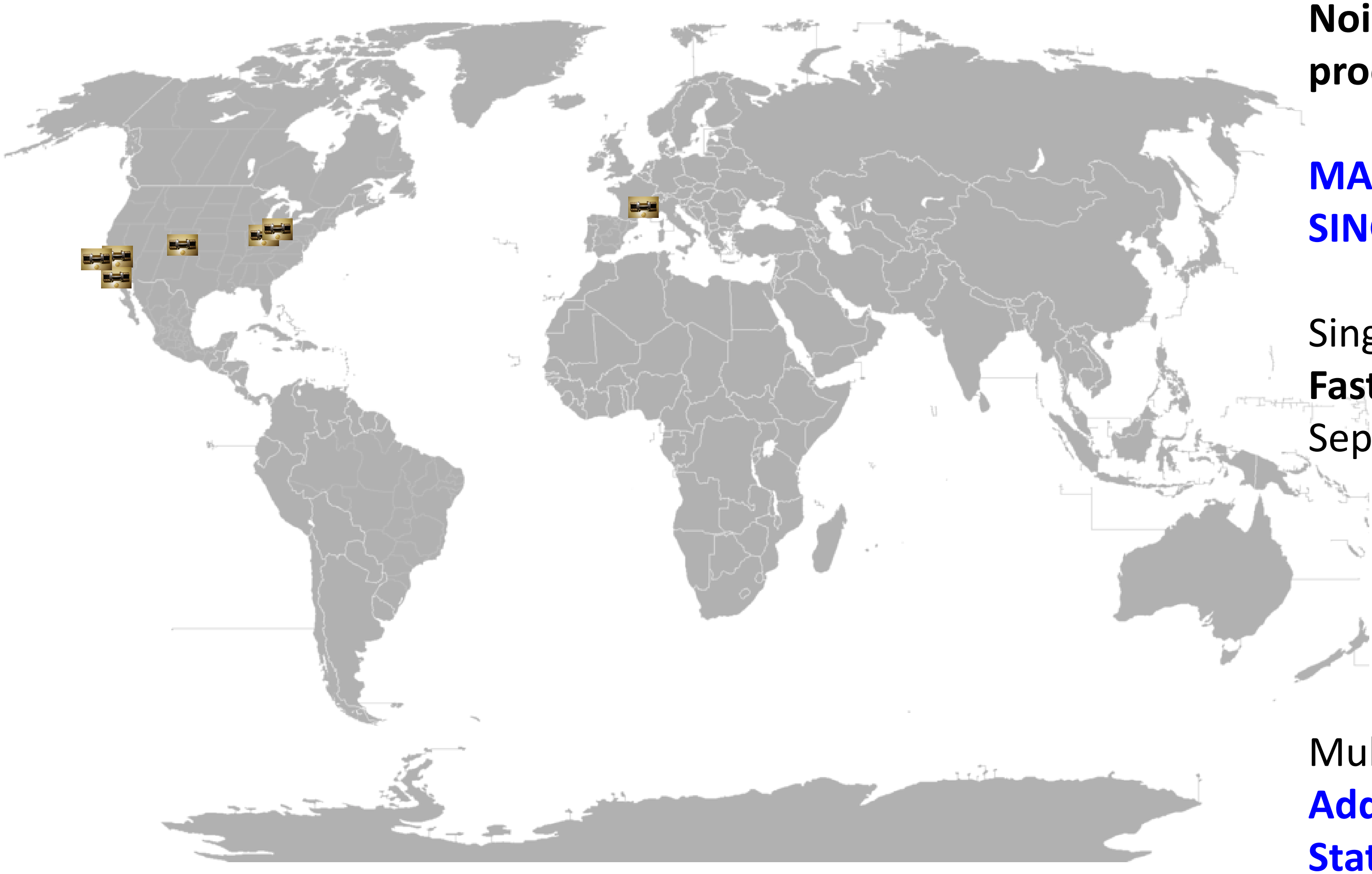
Viodé, RA, et al.
Rapid Commun. Mass Spectrom. 2016, 30, 132–136

SEC/MS incorporating an online ESI charge-detection mass spectrometry

➔**rapid and efficient technique** for the analysis of water-soluble polymers with ultra-high molecular mass in the megadalton range.

➔**attractive solution to the calibration of the size-exclusion chromatography** for very large synthetic polymer analysis, without the use of external standards, most often unrelated to the polymer of interest, or the need for a (sometimes tedious) implementation of a multiple detection configuration.

A road map of CD-MS instruments



Simple but « tricky » (sensitive electronics, **Noise reduction processing)**

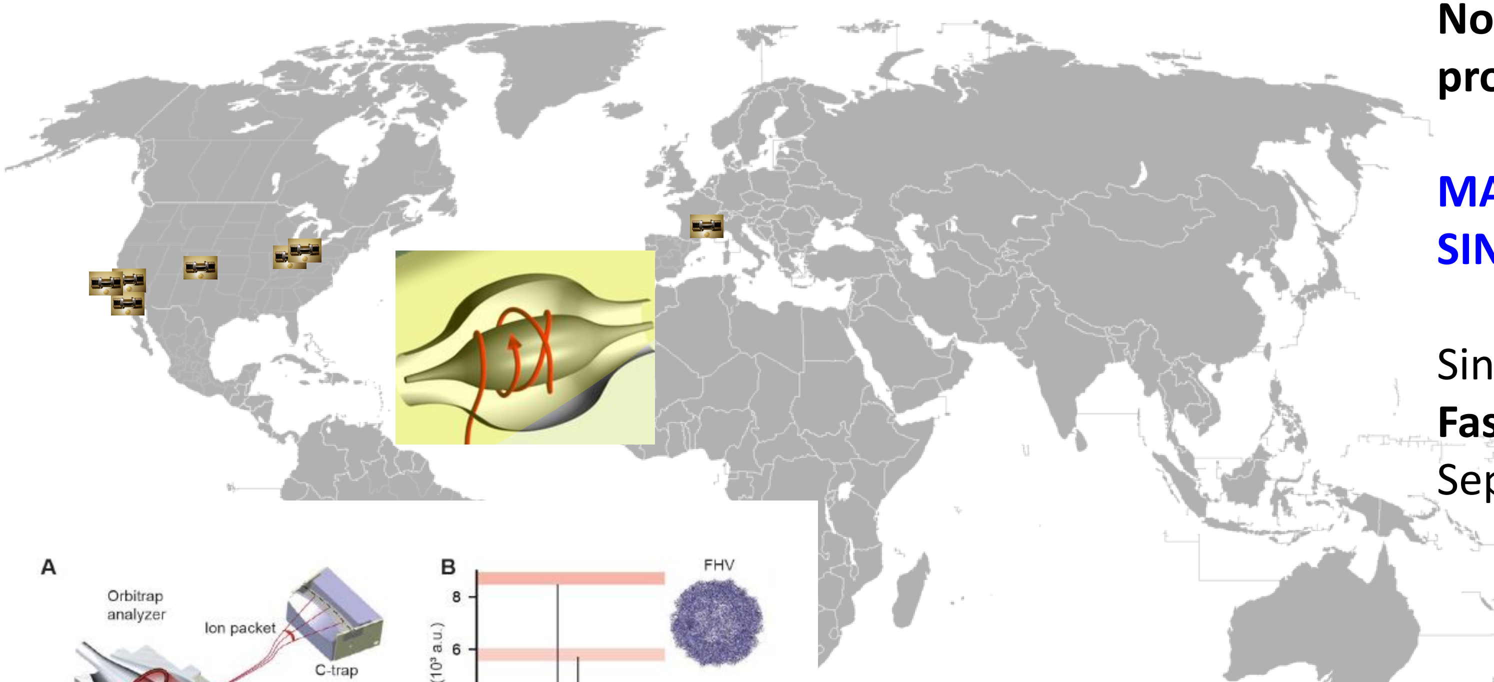
MASS AND CHARGE SINGLE ION LEVEL

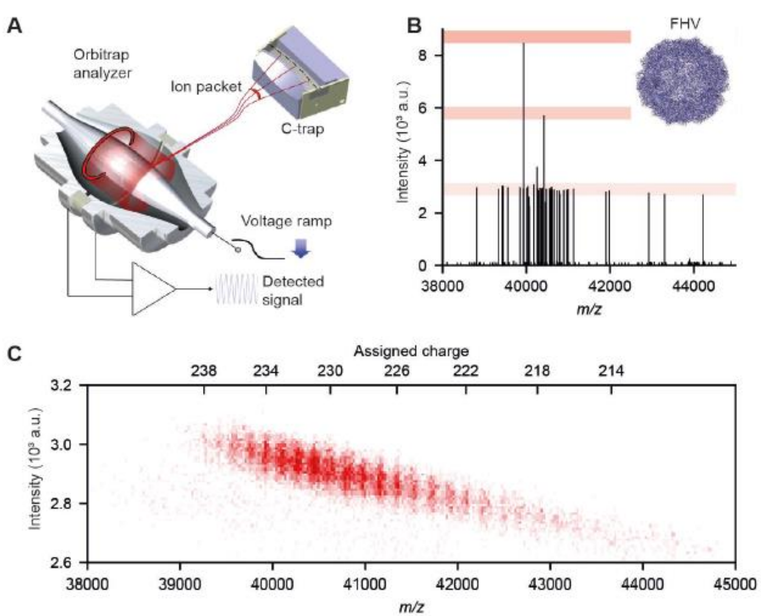
Single pass mode:
Fast and accurate MS
Separative couplings

Multi-pass mode:
Added Value of Statistical Analysis of Individual Events

laser couplings

A road map of CD-MS instruments





Alexander A. Makarov & Albert J.R. Heck
Orbitrap-based single particle charge detection mass spectrometry

Simple but « tricky »
(sensitive electronics, **Noise reduction processing)**

MASS AND CHARGE SINGLE ION LEVEL

Single pass mode:
Fast and accurate MS
Separative couplings

Multi-pass mode:
Added Value of Statistical Analysis of Individual Events

laser couplings

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Mohammad A. HALIM (phD 2015-2017)

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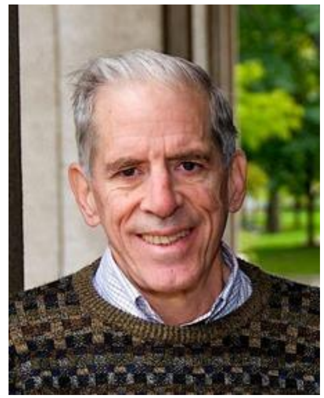
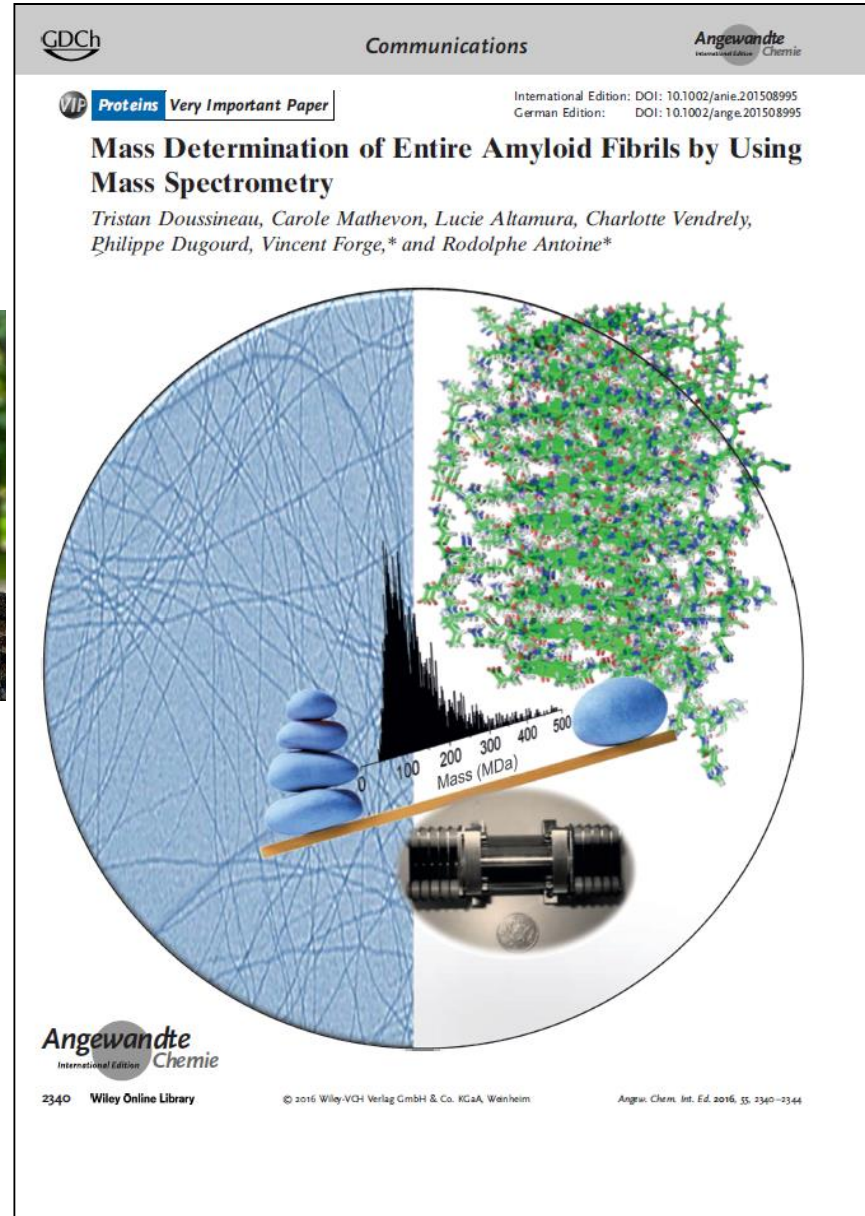
Nesrine OUADAH (Master)
Thomas HAMADA (Master)
Pierre PALETTO (Master)
Arthur VIODÉ (Master)
Caroline BOURGEOIS (Master)
Hussein FAKHOURI (Master)
Aikaterini TSIRKOU (Master)



Robert C. Dunbar (visiting professor at the University of Lyon, summer of 2016) died Oct. 31 2017



GDCh Communications Angewandte Chemie

VIP Proteins Very Important Paper

International Edition: DOI: 10.1002/anie.201508995
German Edition: DOI: 10.1002/ange.201508995

Mass Determination of Entire Amyloid Fibrils by Using Mass Spectrometry

Tristan Doussineau, Carole Mathevon, Lucie Altamura, Charlotte Vendrely, Philippe Dugourd, Vincent Forge, and Rodolphe Antoine**

Angewandte Chemie International Edition

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Prof. Laurence Charles Aix-Marseille Univ. France

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