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

Virus, Nanoparticles, ...

Weighing the nanoworld?

1 kg
1 g
10⁻¹⁴ g
10⁻²⁰ g
10⁻²⁴ g

< ≈10⁻²¹ kg

Mass Spectrometry

10⁻⁹ g

μ-balances

> ≈10⁻¹⁰ kg

NEMS-MS

CHARGE-DETECTION
MASS SPECTROMETRY

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

\[
\frac{m}{z} = \frac{2t^2 K}{L^2}
\]
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 simultaneously recorded with the charge detector.

\[ V = \frac{Z e}{C} \]

**Amplification and Differentiation**

\[ v = f(m/z) \]

**Time-of-Flight (ToF)**

**Velocity v**

L = 37.5 mm

100 charges $\rightarrow$ 1µV

Electronic noise
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

Mirror electrodes

Screen electrodes

Charge detection tube

FFT

frequency (kHz)

time (ms)
<table>
<thead>
<tr>
<th>CDMS mode</th>
<th>Ion count rate (ions/s)</th>
<th>Charge uncertainty (e)</th>
<th>Limit of détection (e)</th>
<th>Mass resolution</th>
<th>Working mass window (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDMS – single pass</td>
<td>1000</td>
<td>50</td>
<td>200-250</td>
<td>5-7</td>
<td>10^6-10^13</td>
</tr>
<tr>
<td>CDMS- array</td>
<td>100</td>
<td>10</td>
<td>100</td>
<td>~10</td>
<td>10^5-10^12</td>
</tr>
<tr>
<td>CDMS- Ion trap</td>
<td>1 (400 ms trapping)</td>
<td>0,65</td>
<td>7</td>
<td>10-100</td>
<td>10^4-10^8</td>
</tr>
</tbody>
</table>
Charge detection mass spectrometry: What do we learn?
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.

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)

**ESI-CDMS**: An efficient complementary tool for NP characterisation

<table>
<thead>
<tr>
<th></th>
<th>monomers</th>
<th>multimers</th>
</tr>
</thead>
<tbody>
<tr>
<td>% free PS beads (N)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>10.7 (140)</td>
<td>56.0 (659)</td>
</tr>
<tr>
<td>ESI-CDMS</td>
<td>8.5 (146)</td>
<td>35.8 (846)</td>
</tr>
<tr>
<td>% clusters (N)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>89.3 (1163)</td>
<td>44.0 (517)</td>
</tr>
<tr>
<td>ESI-CDMS</td>
<td>91.5 (1564)</td>
<td>64.2 (1519)</td>
</tr>
</tbody>
</table>

![Graph showing molar mass vs number of charge](image)

![Image of dodecapods](image)
ESI-CDMS: An efficient complementary tool for NP characterisation
ESI-CDMS: An efficient complementary tool for NP characterisation

Doussineau, RA, et al.
*Journal of the American Chemical Society* **2015** 137 (5), 1929-1937
CDMS, a kind of zetameter?

Dynamic light scattering (DLS) & Zetametry

Electrophoretic mobility ($\mu_{ep}$)

Malvern®, Zetasizer NanoZS

ZETA-POTENTIAL $\zeta$

$r_{Z_{CDMS}, Z_{eff}} = 0.953$

$r_{Z_{CDMS}, Z_{eff}, MW} = 0.74$
Charge-detection Mass spectrometry, and couplings

Separative techniques

Photodissociation techniques
photofragmentation at the single molecule approach

High power CO$_2$ lasers (SYNRAD 25 W)

- **Sudden Loss**
  - Fragment lost
  - Or low-charge fragments ($z<400$ e)

- **Funnel**
  - (bio)polymer « peeling »
  - EVAPORATION

- **Staircase**
  - (asymmetric)
  - FISSION
Size-exclusion chromatography

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

SHODEX column 807 et 806M HQ

Diagram:
- Flow
- Time
- Chromatogram
- Large particles cannot enter gel and are excluded. They have less volume to traverse and elute sooner.
- Small particles can enter gel and have more volume to traverse. They elute later.
SEC-UV & SEC-ESI-CDMS

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

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(sensitive electronics,
Noise reduction
processing)

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laser couplings

Alexander A. Makarov & Albert J.R. Heck
Orbitrap-based single particle charge detection mass spectrometry
Tristan DOUSSINEAU (Post-doc 2010-2014)
Mohammad A. HALIM (PhD 2015-2017)

CongYu BAO (Master)
Marion SANTACREU (Master)
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

Prof. Laurence Charles
Aix-Marseille Univ.
France

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