INSTRUMENTAL TECHNIQUE PRESENTATION

Electrospray Ionization (ESI)

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18/03/2017

Electrospray ionization (ESI)

Method used to produce gaseous ionized molecules from a liquid solution by creating a fine spray of droplets in the presence of a strong electric field.

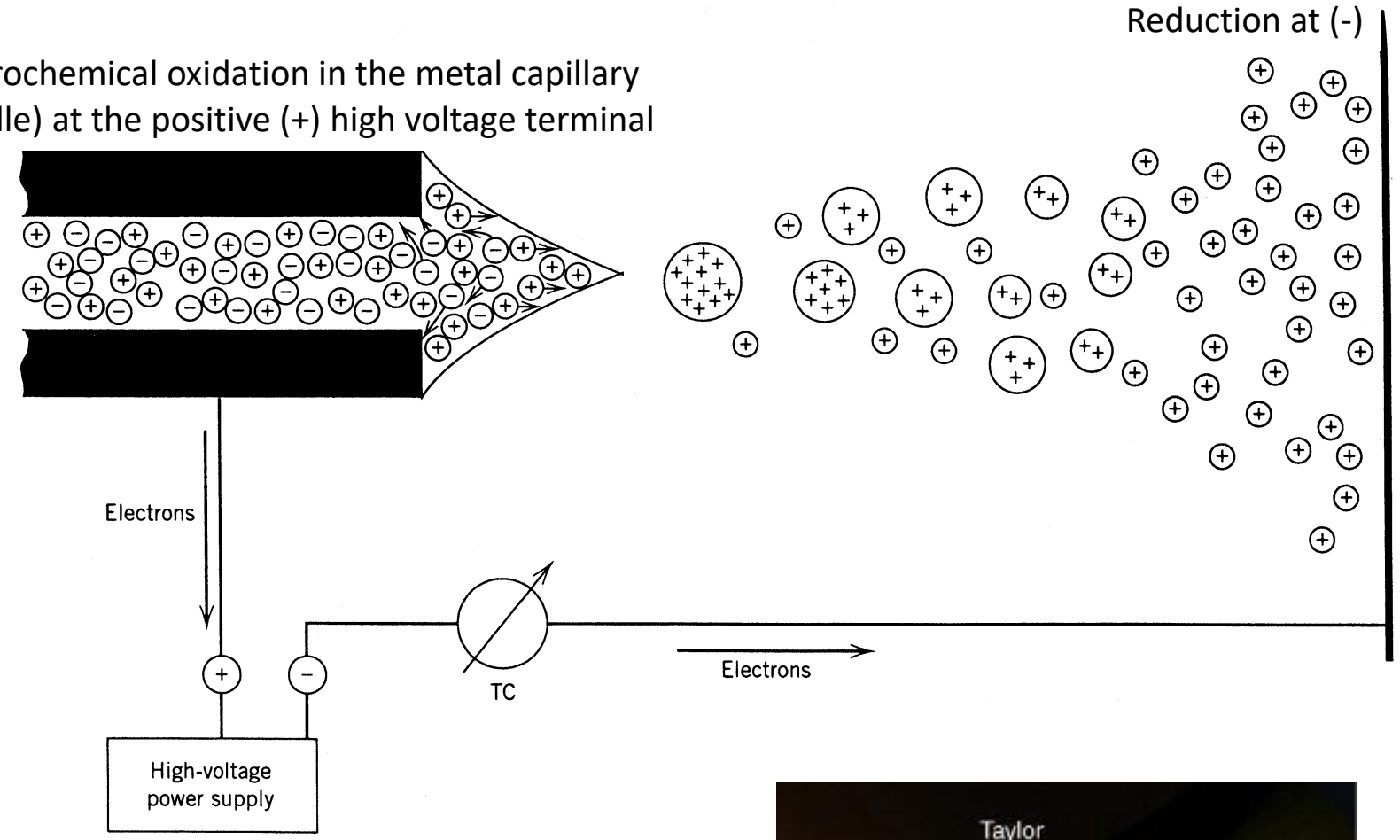
History

Electrospray ionization/mass spectrometry (ESI/MS) which was first described in 1984 (commercial available in 1988), has now become one of the most important techniques for analyzing biomolecules, such as polypeptides, proteins etc.

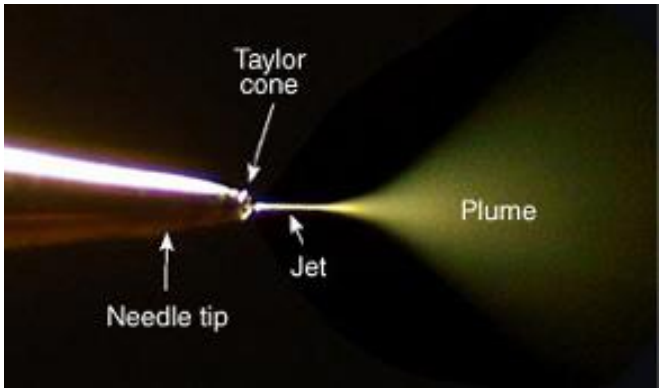
Professor John B. Fenn was awarded the **2002 Nobel Prize in Chemistry** for the development of electrospray ionization mass spectrometry.

Ionization Mechanisms

Electrochemical oxidation in the metal capillary (needle) at the positive (+) high voltage terminal



Electrospray



Electrospray: From solution to gas phase

I. Electrical nebulization of liquid results in the formation of charged micro droplets.

II. Vaporization increases the charge density on the surface of the droplets. Electrostatic repulsion increases.

III. When the electrostatic repulsion exceeds the surface tension the droplet undergoes coulombic fission.

IV. The formation of charged ions in the gas phase.

$$V_{on} = 2 \cdot 10^5 \sqrt{\gamma \cdot r_c} \ln\left(\frac{4d}{r_c}\right)$$

V_{on} : onset voltage for electrospray
d: capillary - electrode distance
r_c: inner diameter of capillary
γ : surface tension of liquid

Parameters Influencing Droplet Size

- The radius (R) of an electrosprayed droplet depends upon fluid density (r), flow rate (V_f), and surface tension (g).

$$R \propto (\rho V_f{}^2 \gamma)^{1/3}$$

- Thus, higher V_f result in larger initial droplet sizes. Larger droplet sizes lead to lower ionization efficiency because the droplets are not so close in size to the Rayleigh limit

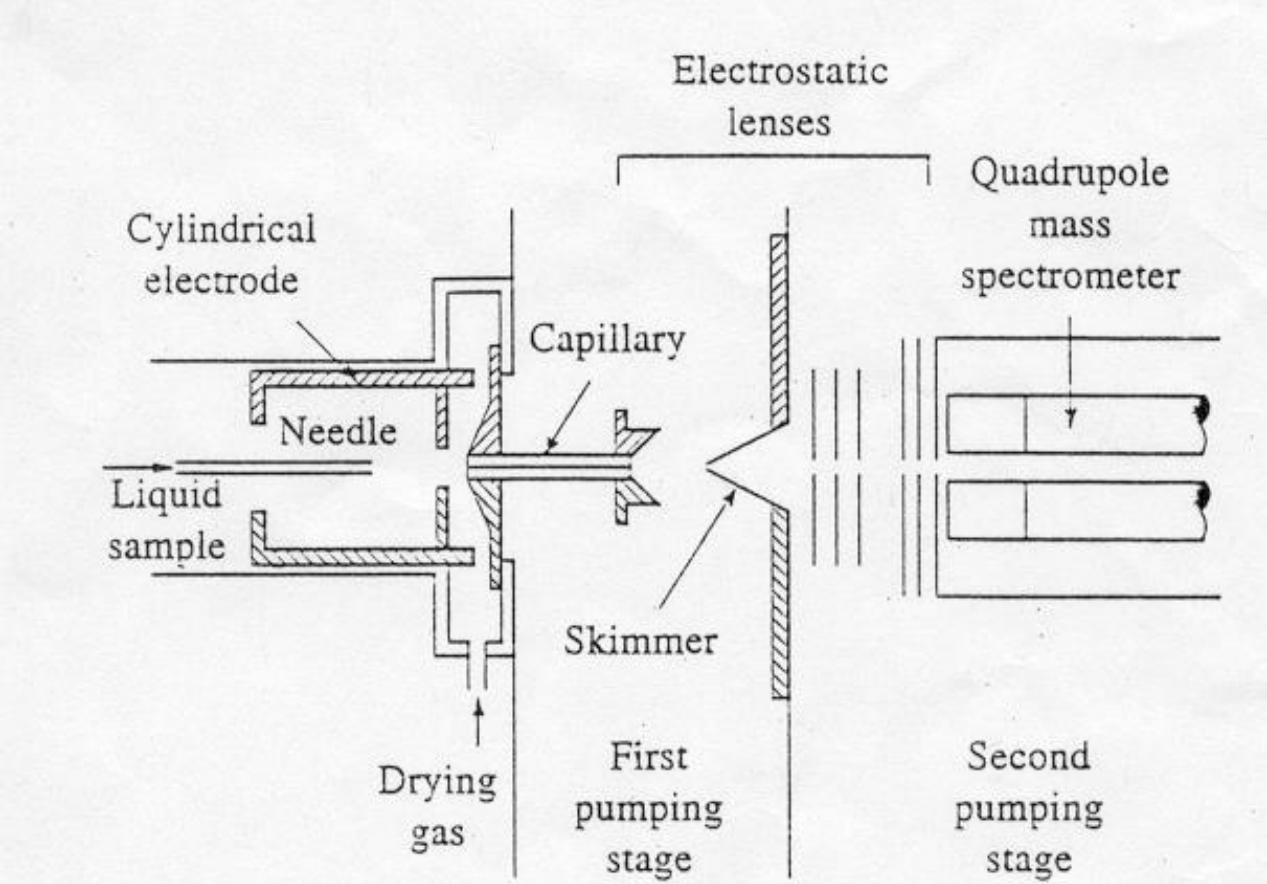
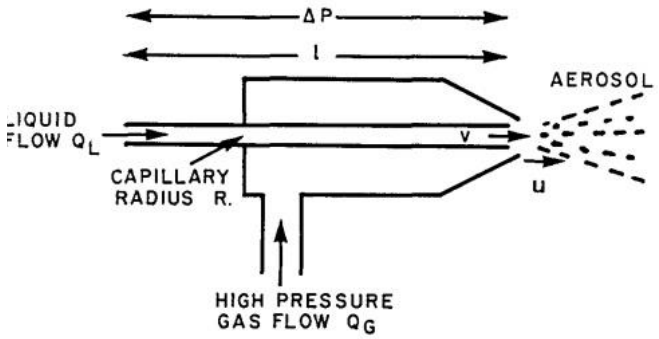
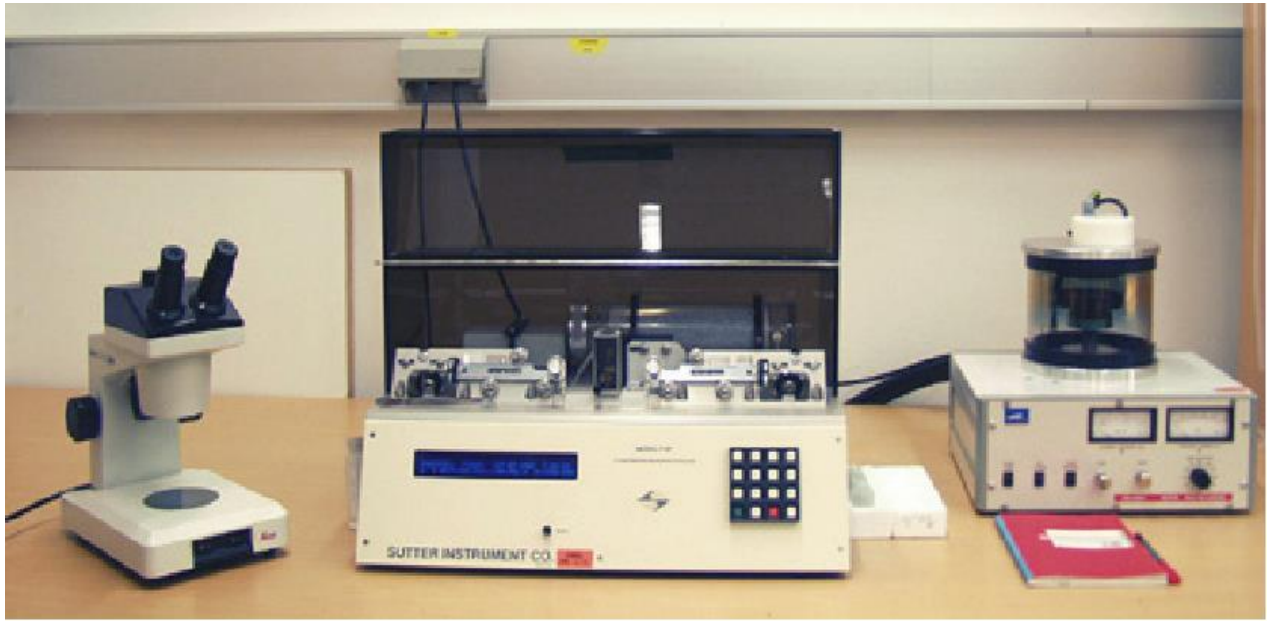


Figure 20-8 Apparatus for electrospray ionization. *(From J. B. Fenn et al., Science, 1989, 246, 65.)*

ESI Source:



Nano-Electrospray



- Flow rates of 10-40 nL/min (25-100 min analysis time)
- Sample volumes down to 300 nL
- Near 100 % sample utilization
- Minimal instrument contamination
- Spray from 0% to 100% aqueous solvents

Nano ES vs. conventional ES

Electrospray parameters	NanoES	Conventional ES
Capillary	1-3µm	>100µm
Flow	10-40nL/min.	>500nL/min.
ES voltages	300-700V	>2500V

Droplets	NanoES	Conventional ES
Radius	50 - 200nm	1000 - 2000nm
Volume	$5 \cdot 10^{-13}$ - $4 \cdot 10^{-12}$µL	$4 \cdot 10^{-9}$ - $3 \cdot 10^{-8}$µL
Analyte molecules per droplet (at 1pmol/µL)	0.3 - 2.5	$2.5 \cdot 10^{3}$ - $1.9 \cdot 10^{4}$

ESI Advantages

- Soft-ionization technique
- Controllable fragmentation
- Readily coupled to liquid separations
- Produces intact non-covalent complexes
- Multiple-charging of analyte
- Capable of ionizing large molecules (to MDa)

Ionization techniques

Ionization Method	Typical Analytes	Sample Introduction	Mass Range	Method Highlights
Electron Impact (EI)	Relatively small. Volatile.	GC or liquid or solid probe	To 1000 Daltons	Hard method. Provides structural info
Chemical Ionization (CI)	Relatively small. Volatile.	GC or liquid or solid probe	To 1000 Daltons	Soft method. Molecular ion peak $[M+H]^+$
Electrospray (ESI)	Peptides/proteins. Non-volatile.	Liquid Chromatography	To 200,000 Daltons	Soft method. Ions often multiply charged.
Matrix Assisted Laser Desorption (MALDI)	Peptides/proteins. Non-volatile.	Sample mixed in solid matrix	To 500,000 Daltons	Soft method. Very high mass range.
Fast Atom Bombardment (FAB)	Carbs/peptides. Non-volatile.	Sample mixed in viscous matrix	To 6000 Daltons	Soft method, but harder than ESI or MALDI

..... Thank You .....