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Development of an HILIC-ESI-MS method for lanthanide speciation in nuclear fuel treatment processes

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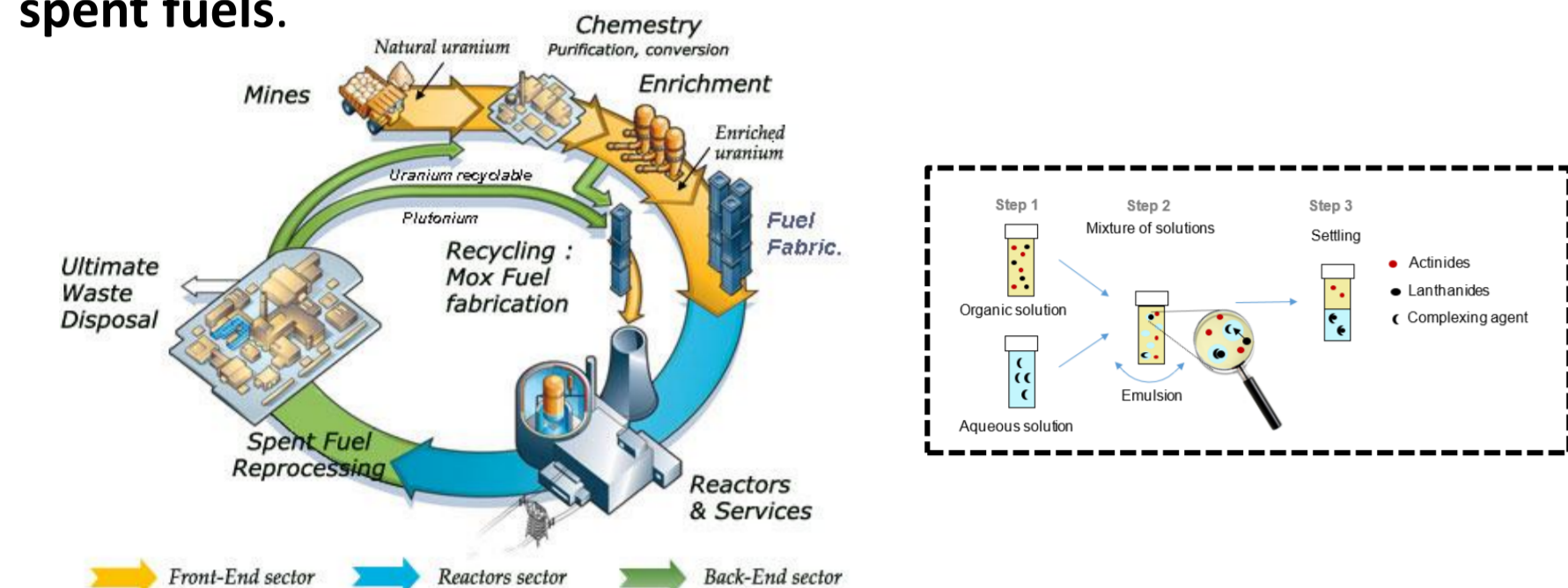
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Introduction

Context:

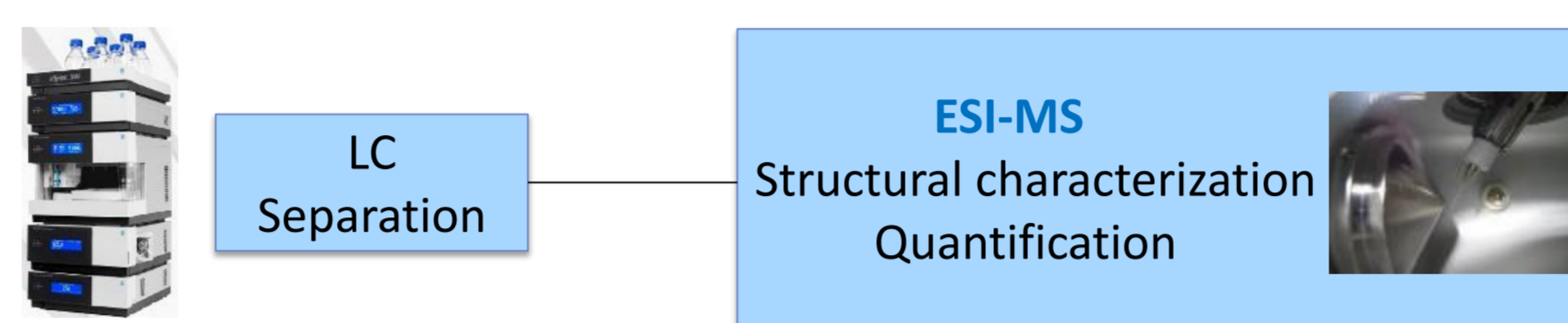
Research on the sustainable management of radioactive materials and waste has led to dedicated **treatment processes based on liquid-liquid extraction**, aiming at **selectively recover targeted radionuclides** including **lanthanides (Ln) and actinides (An)**, from **current or future spent fuels**.



Radionuclide speciation analysis at various key points is essential to obtain **fundamental data** in order to **better understand the mechanisms** governing these treatment processes and to **assess/improve their performance**.

Objectives:

The aim of this work is to **develop a Ln speciation analysis method** by **hydrophilic interaction liquid chromatography (HILIC) [1] coupled to electrospray ionization - mass spectrometry (ESI-MS)**.



- Minimization of the effluent production** while maintaining **efficient and rapid separations**.
Topic of major concern in nuclear applications
Reduce, Replace, Recycle
- Structural characterization** of lanthanide complexes by ESI-MS.
Speciation information

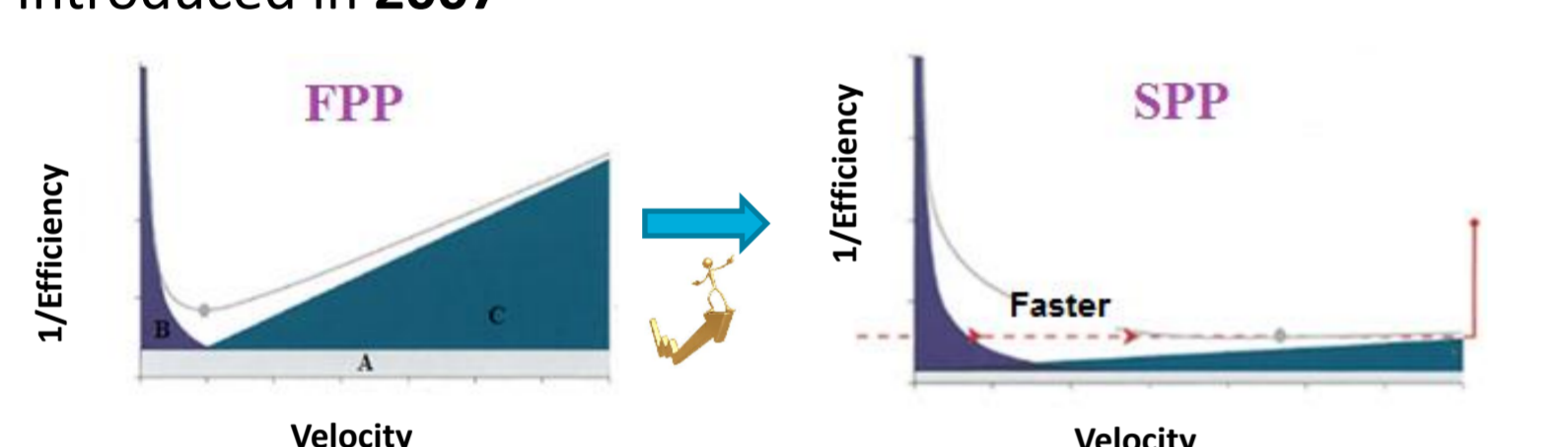
Generic methodological approach:

- Composition of model samples**
 - Lanthanides:** [Table of Lanthanide elements: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu]
 - Polyaminocarboxylic acids:** back extraction agents of An/Ln
 - EDTA
 - DTPA
- Formation of Ln complexes: hydrophilic, polar and ionic**
- Hydrophilic interaction chromatography (HILIC) mode** was selected to separate them [2].
- Background**
 - A combination **stationary phase/mobile phase** was set up:
 - Amide functionalization
 - 70/30 (v/v) acetonitrile/water
 - [NH₄CH₂COO] = 15 mmol.L⁻¹
 - 0.5 % formic acid

Results

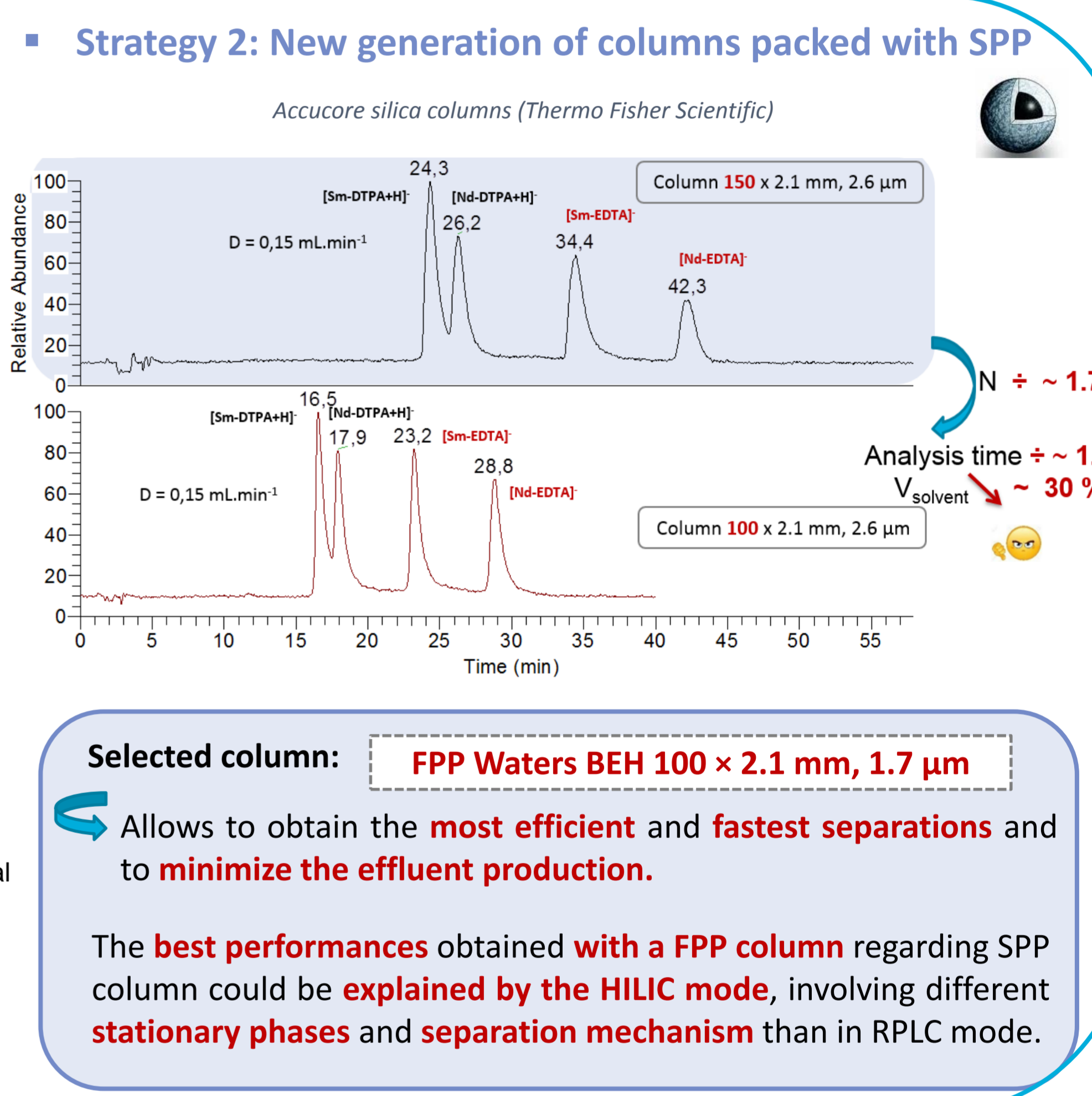
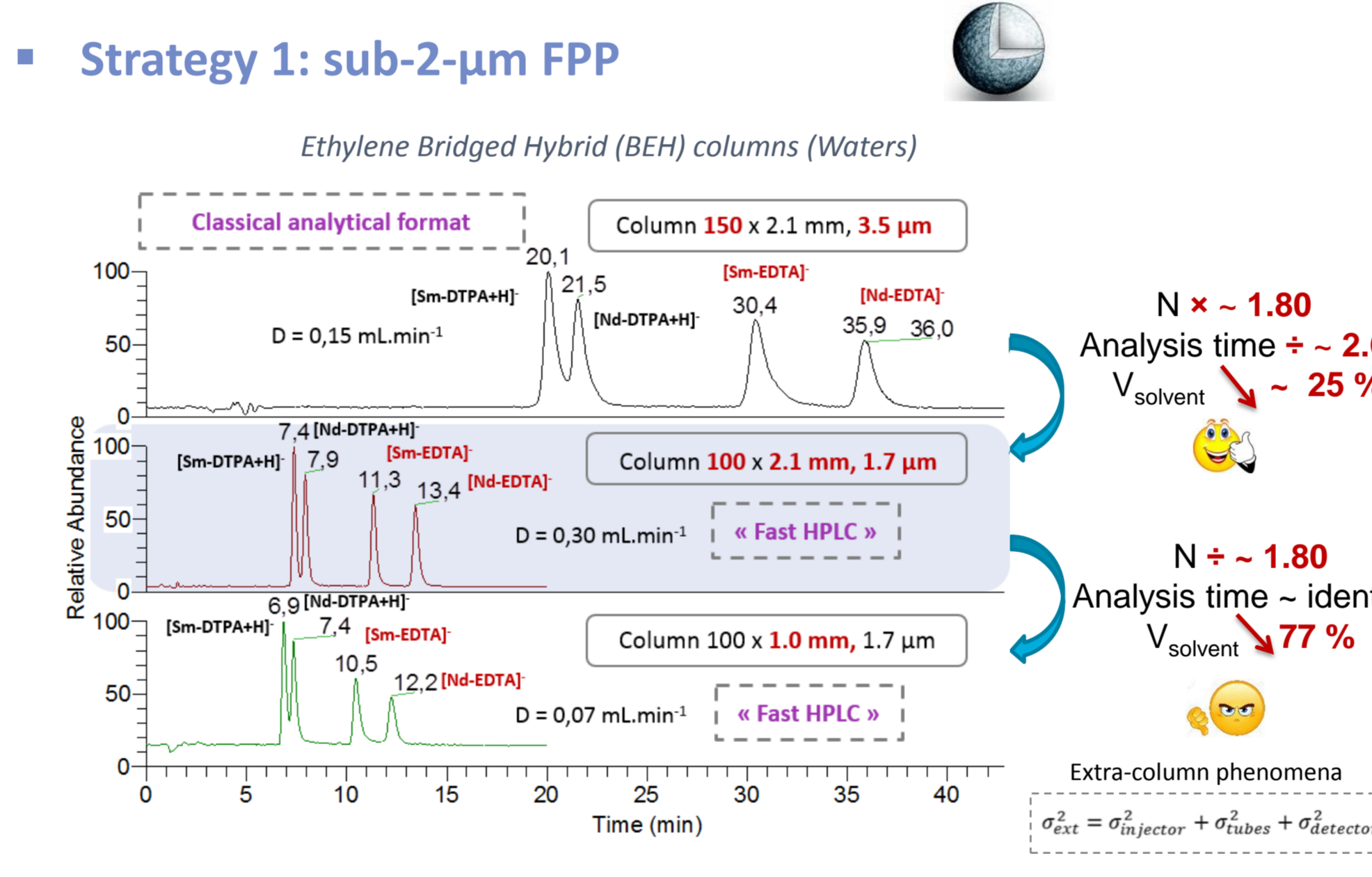
1 Minimization of the effluent production while maintaining efficient and rapid separations

- Two strategies according "Fast HPLC" approach [3-4]:**
 - Reduction the geometrical parameters** of columns (length L and internal diameter d_i) and the **particle size** (d_p sub-2-µm)
Sub-2-µm fully porous particles (FPP) introduced in 2004, employed in many application fields
 - New generation of column packed with superficially porous particles (SPP)**
Introduced in 2007



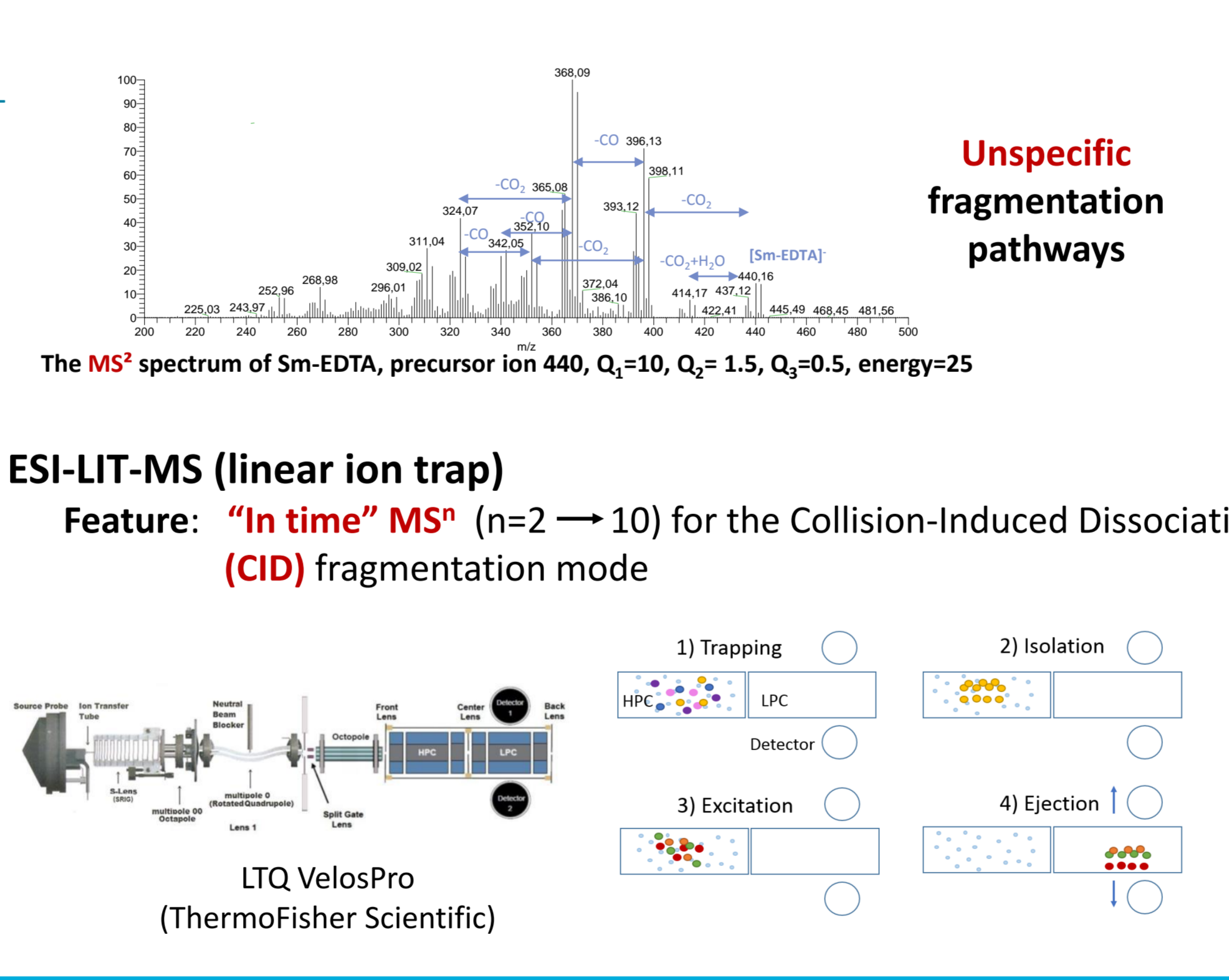
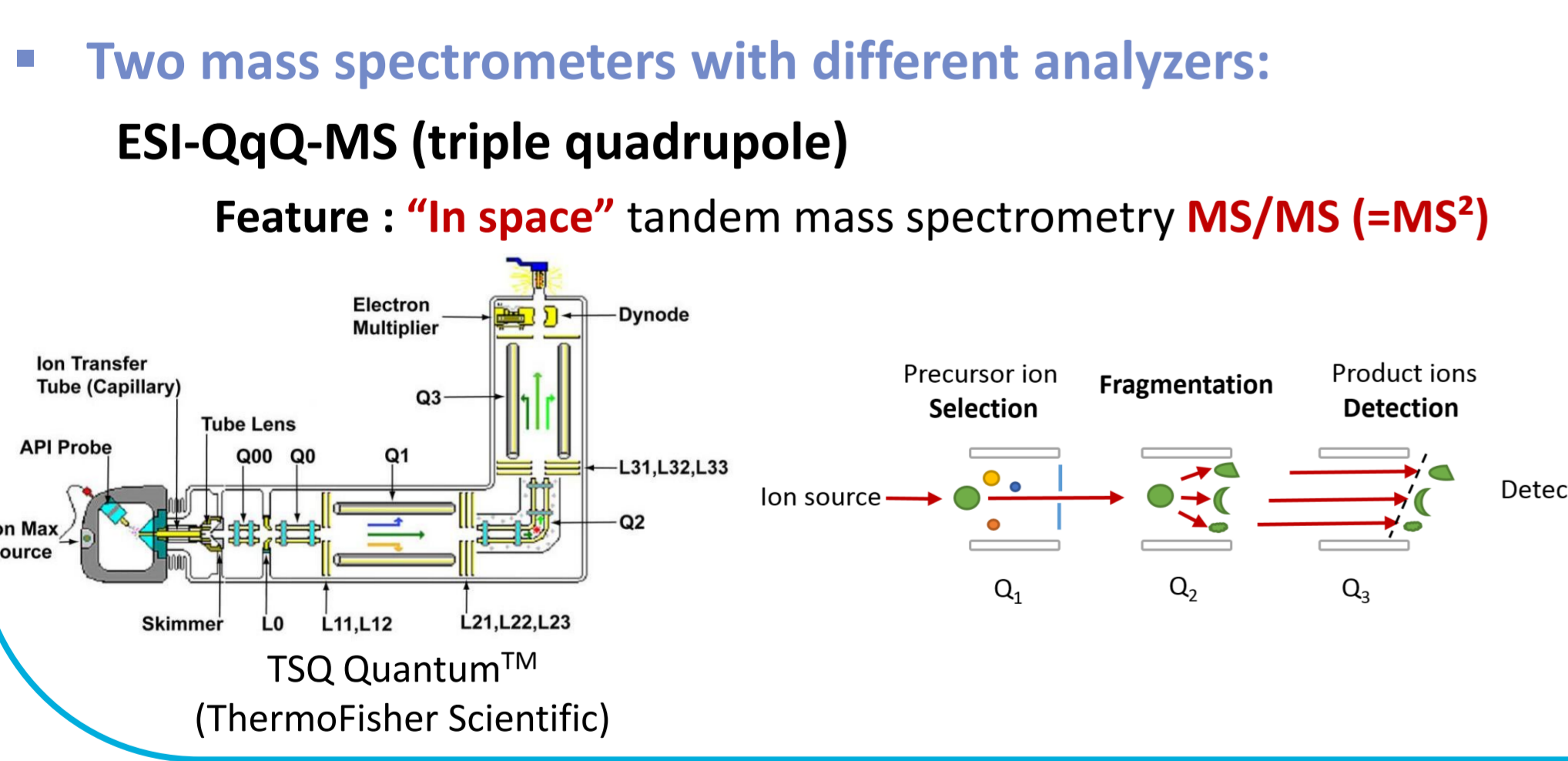
Rapid mass transfer → **efficiency maintained at high flow-rates**
FPP and SPP columns with the same L, d_i and d_p
Expected efficiency (N) ↑ 60%, analysis time ÷ 2, V_{solvent} ↓ 45% with SPP columns in Reversed Phase Liquid Chromatography (RPLC) [5].
However, available **stationary phases for HILIC mode are restricted**

- Selection criteria:**
 - Conditions to achieve the **best trade-off** between:
 - Efficiency of separation N
 - Analysis time
 - Solvent consumption → effluent production



2 Structural characterization of lanthanide complexes by ESI-MS

- Soft ionization technique**, allows maintaining the **integrity of species**
 - Identification of species
 - Structural characterization
- Sm-EDTA complex → [Sm-EDTA]⁻ in ESI(-)
- According the technologies of the instruments, **elemental and molecular information** during the **same analysis** can be obtained [6].



Conclusion/Perspectives

- Conclusion:**
- "Fast HPLC" conditions with the FPP Waters BEH column (100 x 2.1 mm, 1.7 µm) allow to obtain the **most efficient and fastest separations** and to **minimize the effluent production** compared to SPP columns.
 - The **identification of fragmentation pathways** of Ln complexes allows:
 - Structural characterization → speciation information
 - To collect data that will be helpful to identify unknown species in real samples

- Perspectives:**
- To develop **accurate quantification methods** of Ln contained in complexes by HILIC ESI-MS
 - To transpose the **methodological and instrumental developments** in glove box for **radioelement speciation analysis**
 - To extend this methodological approach to **other treatment processes** and the associated samples

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