THE POSSIBILITIES OF NANOFIBERS FOR EXTRACTION OF BIOLOGICALLY ACTIVE COMPOUNDS IN CHROMATOGRAPHY

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Outline:

- On-line solid-phase extraction principles in chromatography
- Nanofibers and fabrication procedure for the efficient extraction
- Practical aspects and pitfalls of on-line nanofibrous extraction
- Nanofibers as alternative to restricted access materials
- Future perspectives and conclusion

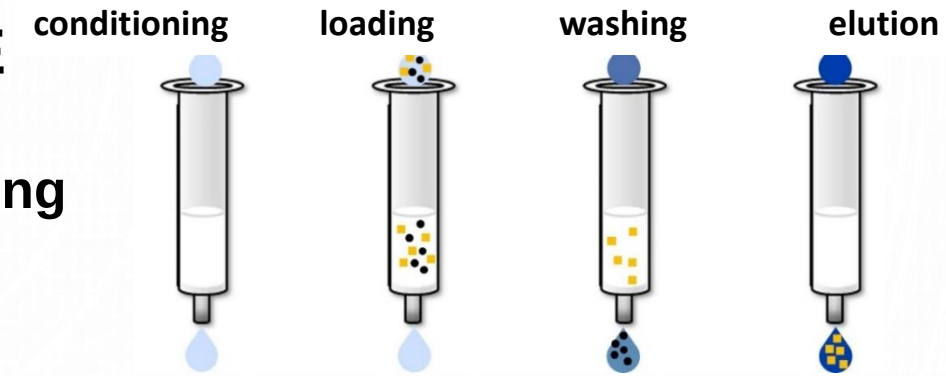
SOLID PHASE EXTRACTION

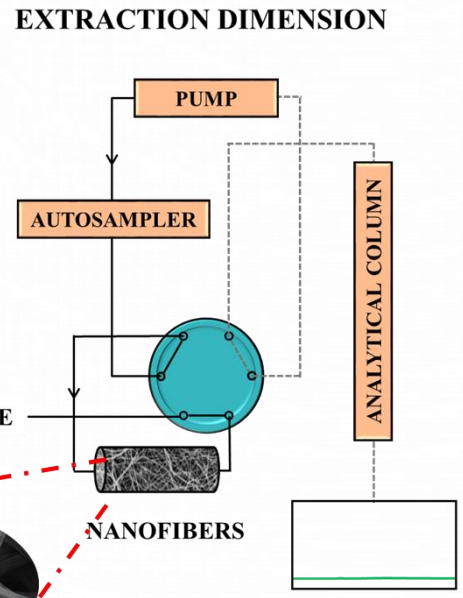
„COLUMN SWITCHING“ (on-line SPE)

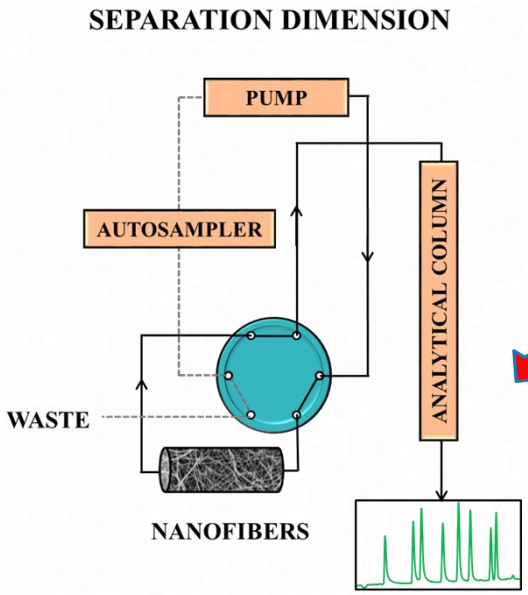
- Fastening the analysis
- Preconcentration
- Low solvent consumption
- Automation

OFF-LINE SPE

- Time-consuming
- Tedious



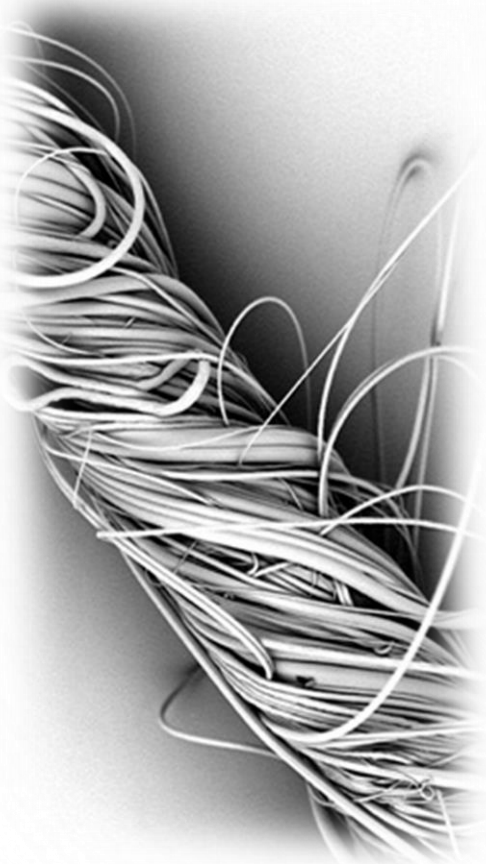




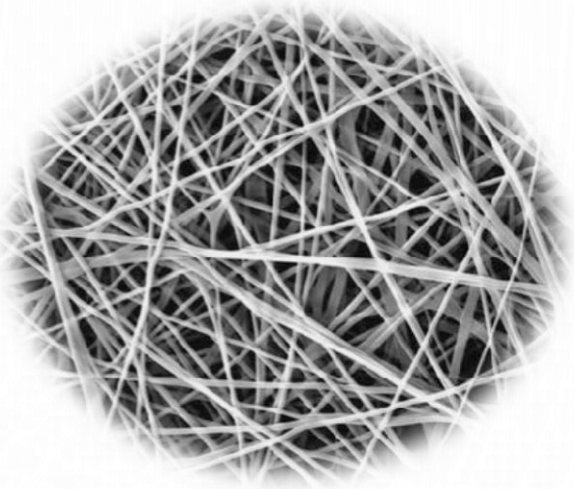
Step 1:
Sample loading on extraction column
Clean-up, preconcentration

Step 2:
Elution onto the analytical column
Chromatographic separation

NANOFIBERS



- Advanced extraction sorbents with high potential



- Large surface area to volume ratio for extraction

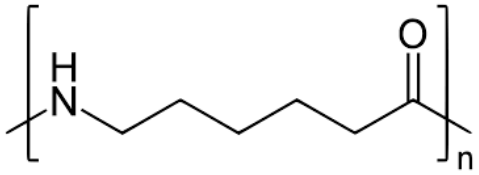
- **High adsorption capacity**
- **High preconcentration factor**

- **Variability of properties**
  - functionalization of nanofibers, coating
  - combination of nanofibers with microfibers
  - different types of production

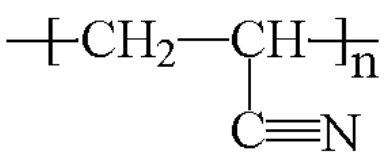
Nanofibers - a material that can be used in a wide range of extraction methods.

Nanofiber polymers as extraction phases

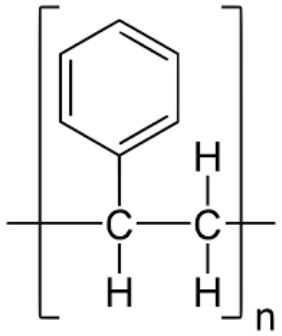
Synthetic polymers:



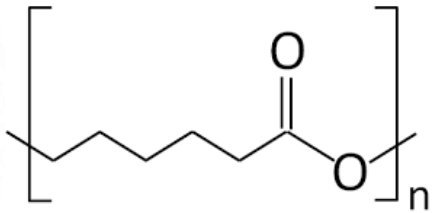
Polyamide 6 (PA-6)



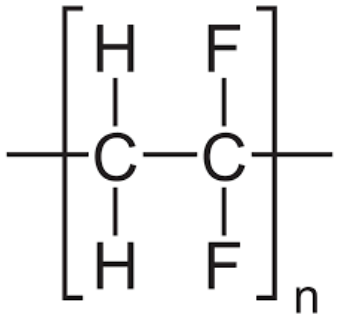
Polyacrylonitrile (PAN)



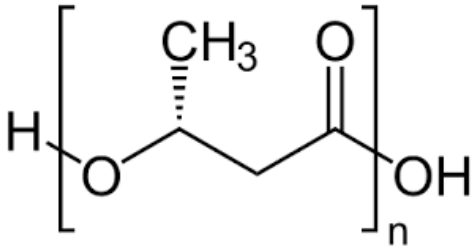
Polystyrene (PS)



Polycaprolactone (PCL)



Polyvinylidene fluoride (PVDF)

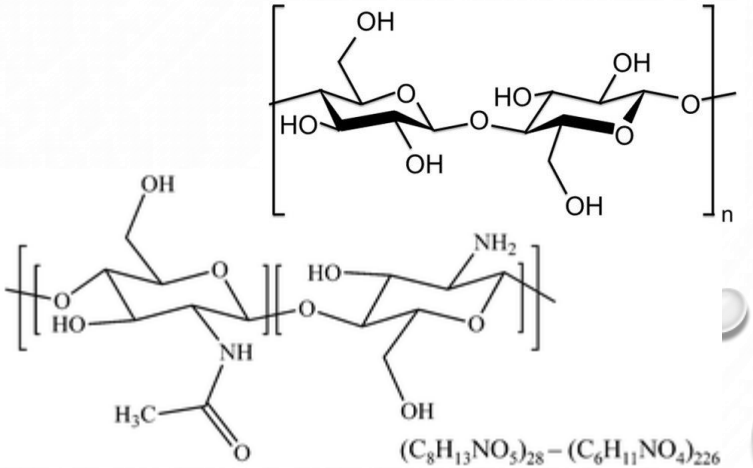


Polyhydroxybutyrate (PHB)

Bio-polymers:

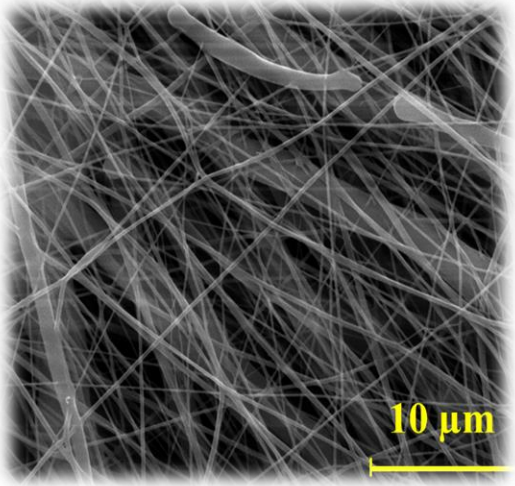
Large potential in biomed. applications.
Low stability (10-30 extraction cycles).
Not repeatable results.

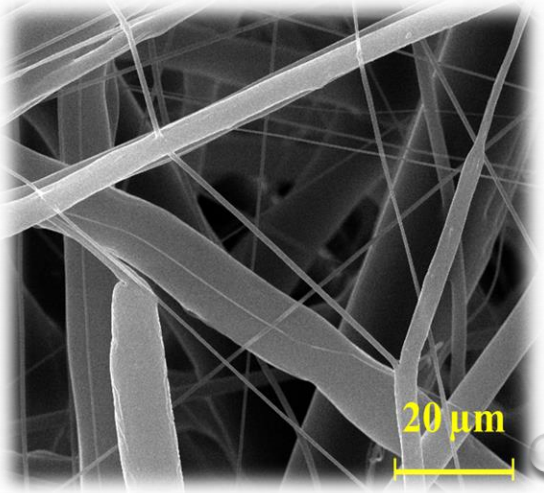
Cellulose and chitosan-based nanomaterials



Nanofibers fabrication procedure

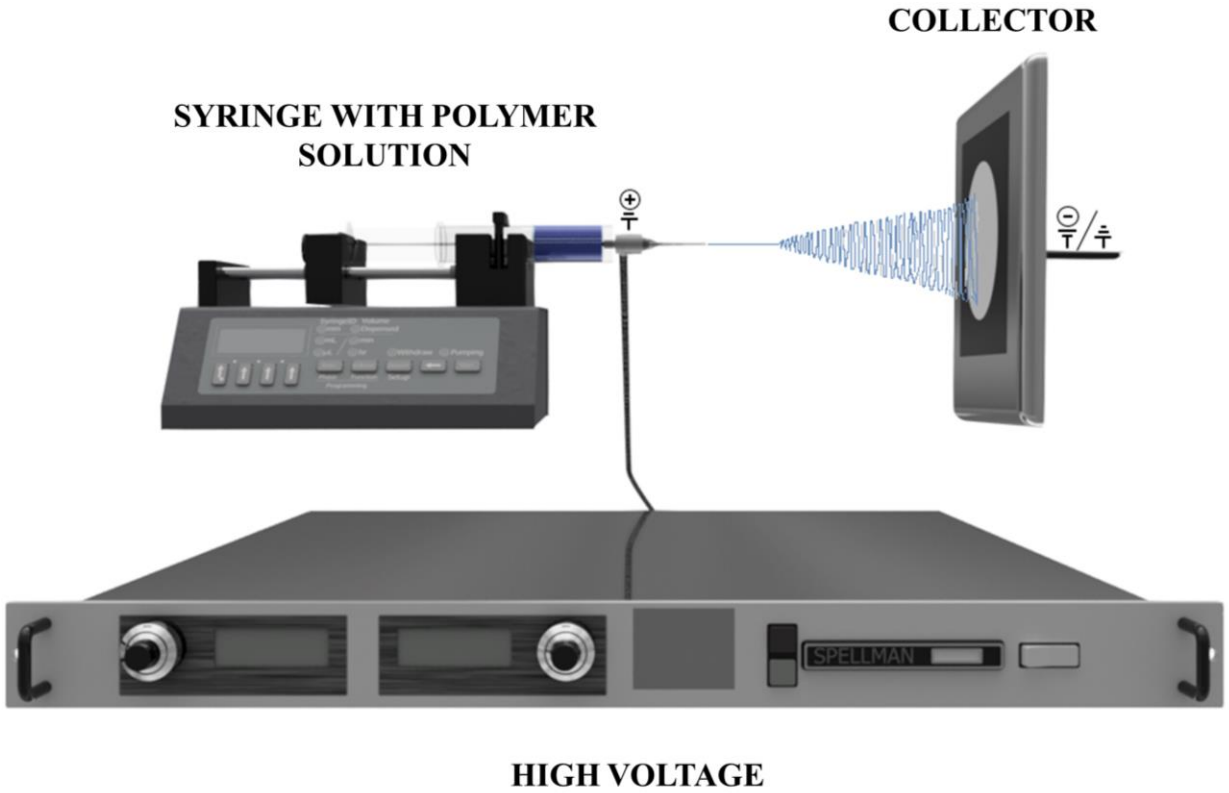
Extraction efficiency and mechanical stability in HPLC





FABRICATION OF NANOFIBERS BY ELECTROSPINNING

Direct current vs. alternating current



Direct current vs. alternating current electrospinning

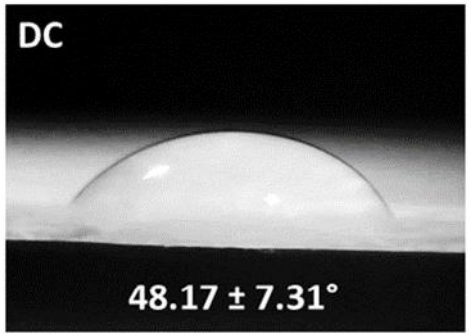
Direct current limitation

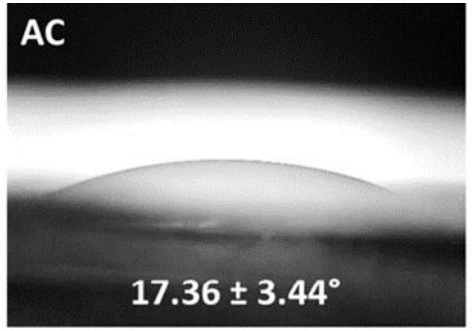
- Thin layer
- Limited porosity (collapse of structure)
- Difficult packing

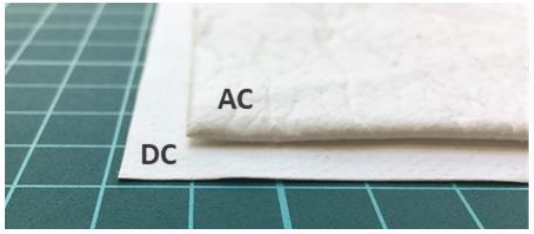
Alternating current:

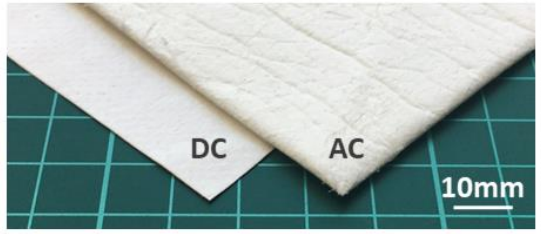
- High surface density
- Thickness of sheet
- Larger pore size
- **Wettability**

Contact angle

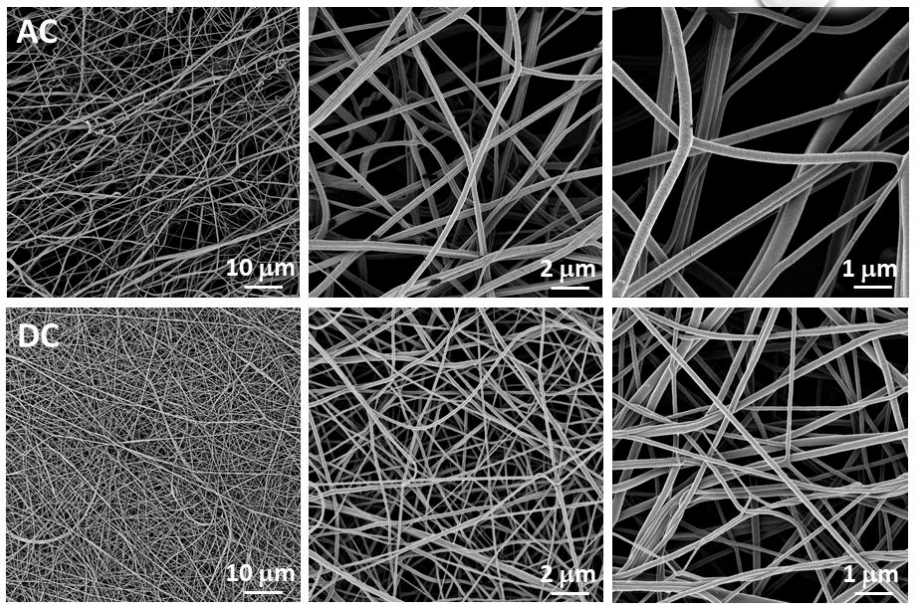




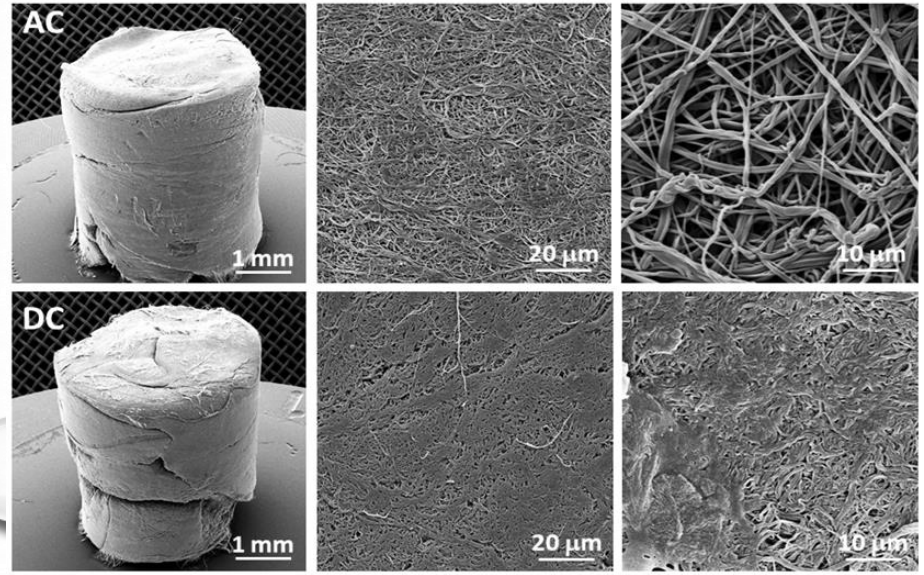




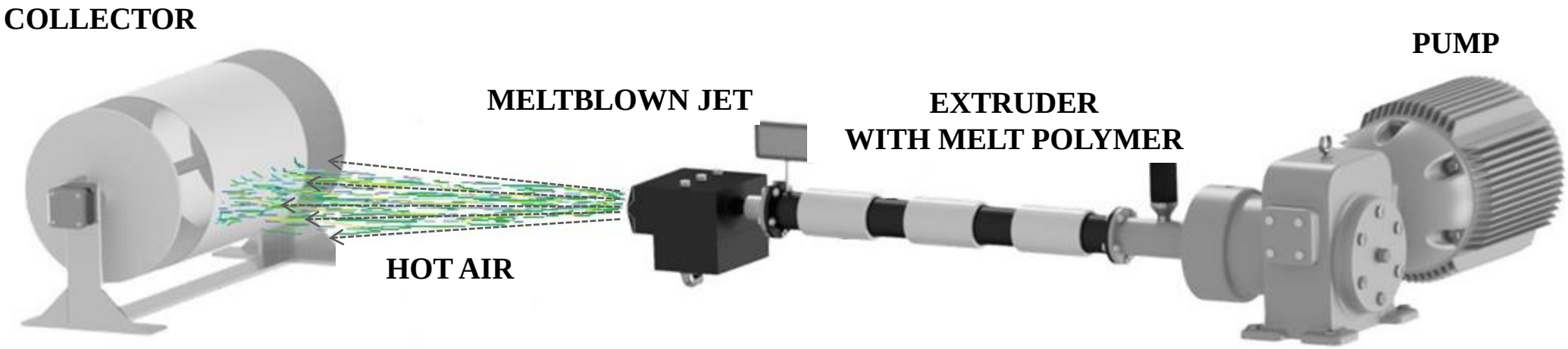
Before on-line SPE

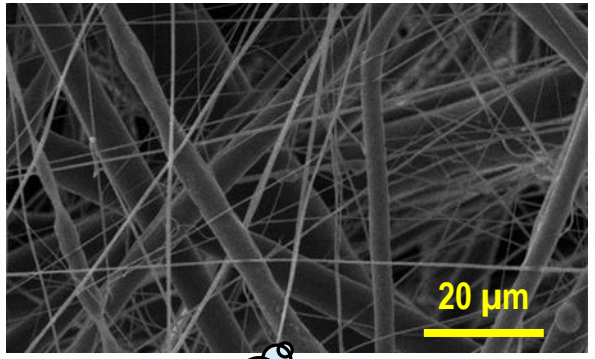


After on-line SPE



FABRICATION OF NANOFIBERS BY MELTBLOWN PROCEDURE





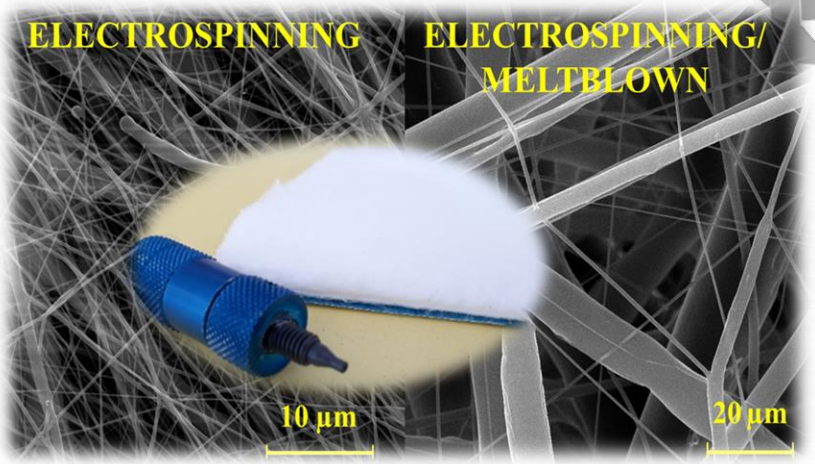
Micro vs. Nano

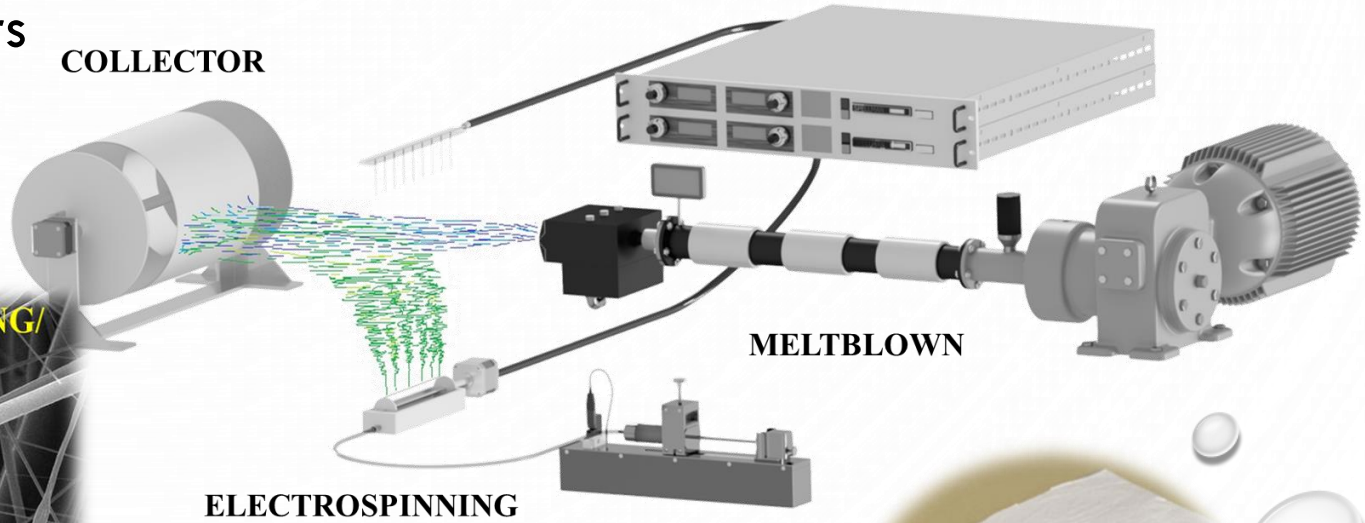
Composite nanofibers - meltblown with electrospinning

Mixed nanofibers:

Electrospinning with meltblown coupled to one technique

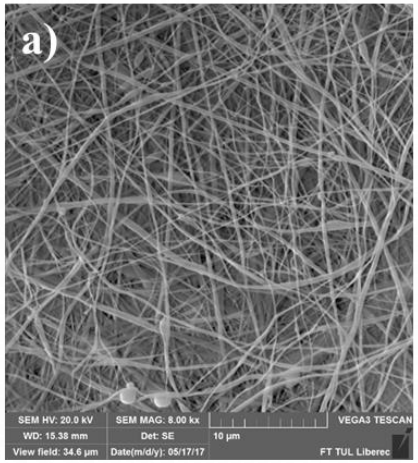
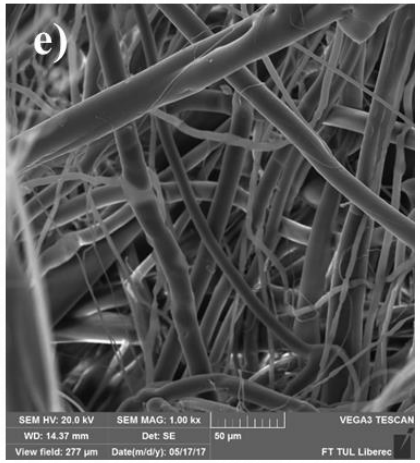
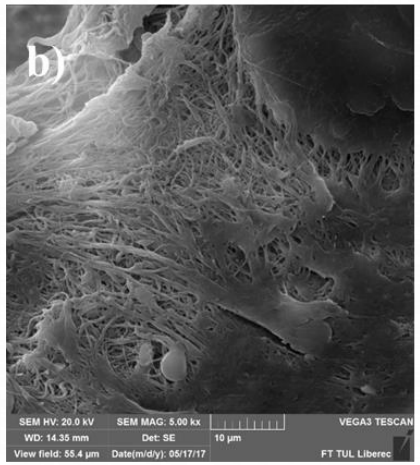
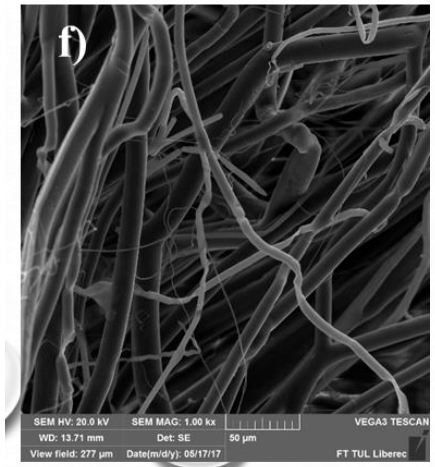
- two same or different polymers
- technology of 3D structured (cotton-like material)
- microfibers as scaffold for nanofibers
- **mechanically stable**
- and highly porous structure





A comparison study of simple and composite nano/microfiber polymers

Mechanical stability in a high-pressure chromatography system

	PVDF	PCL/PVDF
Before on-line SPE		
After on-line SPE		

PRACTICAL ASPECTS AND PITFALLS OF NANOFIBROUS EXTRACTION

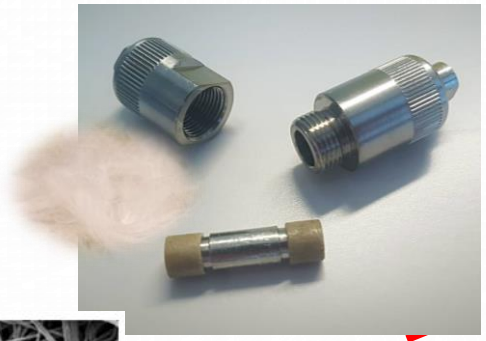
- **Good repeatability of the packing process requires specific practical skills**
- Packing of nanofibers - important factor for (recovery/repeatability)
- Cotton-like nanofiber materials (3D) is simpler than using the 2D sheet nanofiber
- Cartridges must be prepared with minimal void volumes

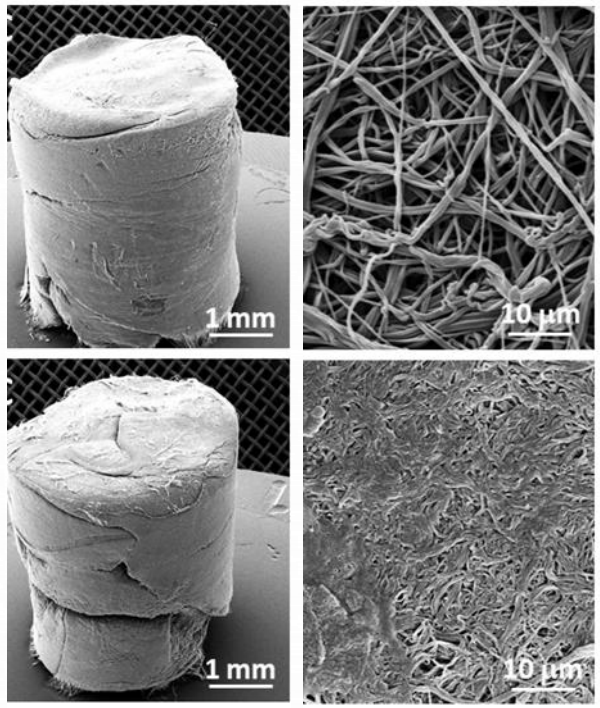
COLUMN PACKING – PRACTICAL ASPECTS

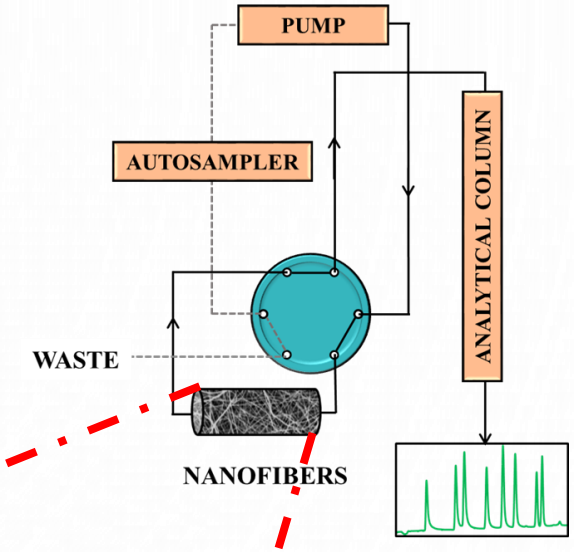
Optimization of the nanofibrous on-line SPE HPLC/UHPLC method is not a trouble-free procedure

Problems:

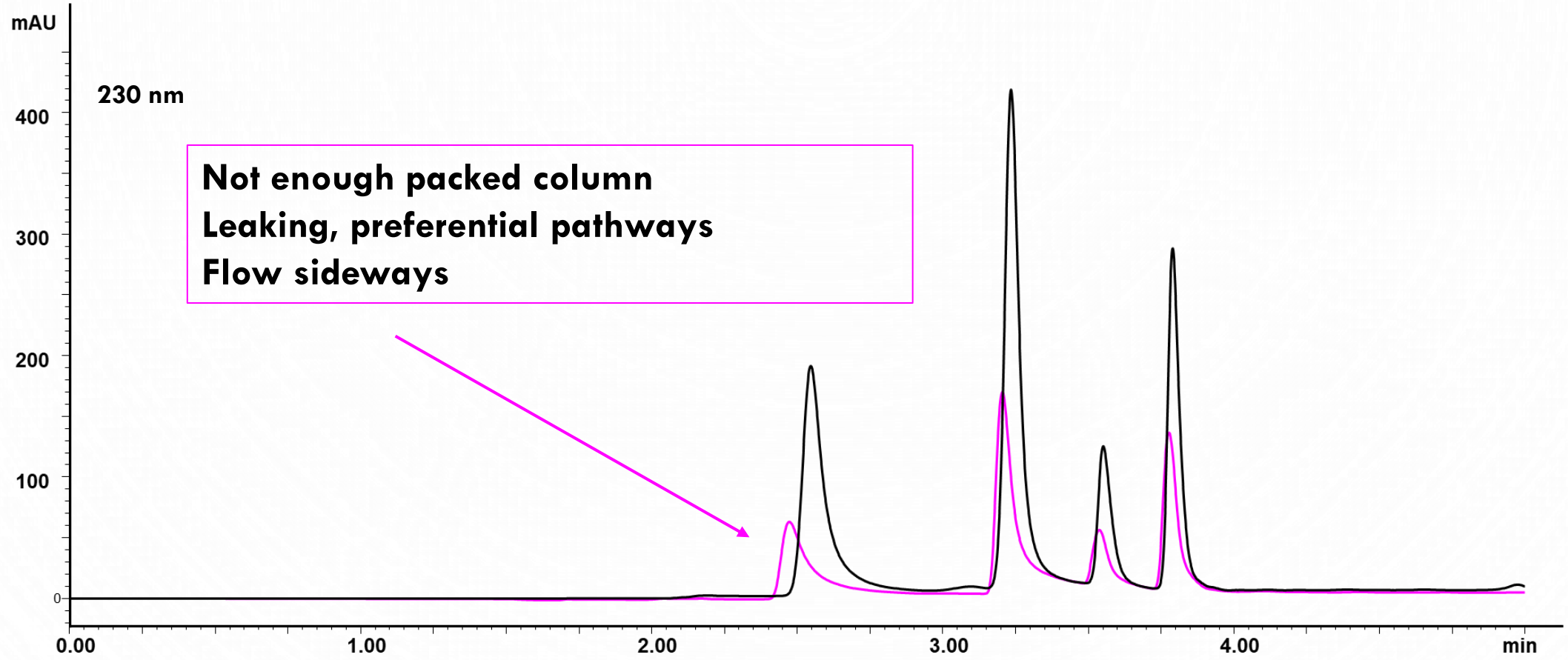
- **exceeding the pressure limits!**
- leakage from the cartridge
- pressure fluctuations
- flow inconsistency
- nanofibers pressurization
- mechanical degradation







Packing of nano-SPE column – „bad“ and „worse“



NANOFIBERS AS „RESTRICTED ACCESS MATERIALS“

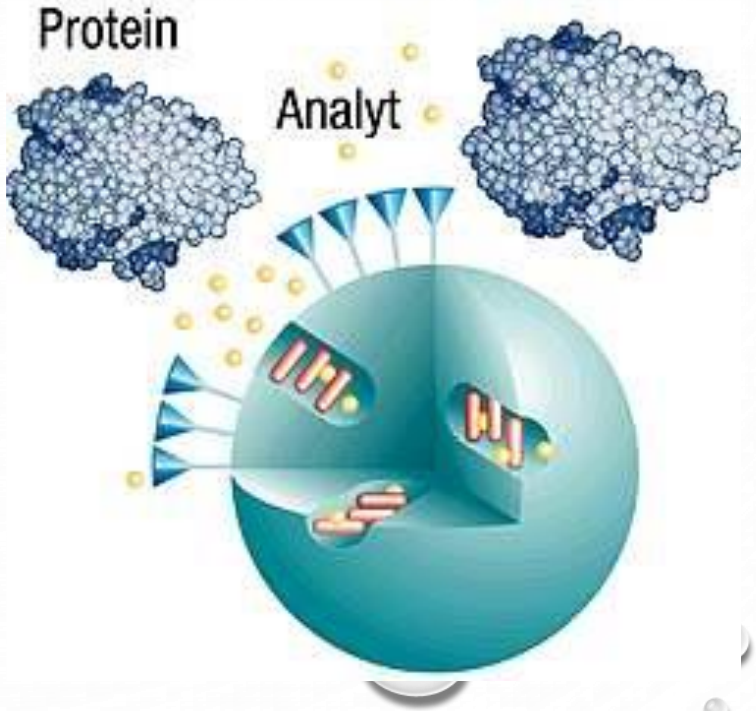
FOR THE CLEAN-UP OF THE PROTEIN MATRIX

Restricted access materials (RAM)

- Direct and repetitive injection of complex biological samples/protein matrix to on-line SPE/HPLC system

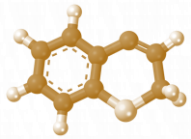
- External hydrophilic surface:
    - Removing macromolecular proteins

- Internal hydrophobic surface:
    - Retention of low molecular analytes



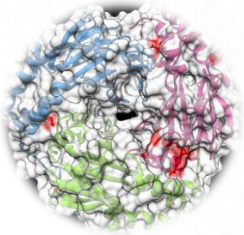
Simulation of restricted access material function with using nanofibers

- ✓ **High surface area to volume ratio**

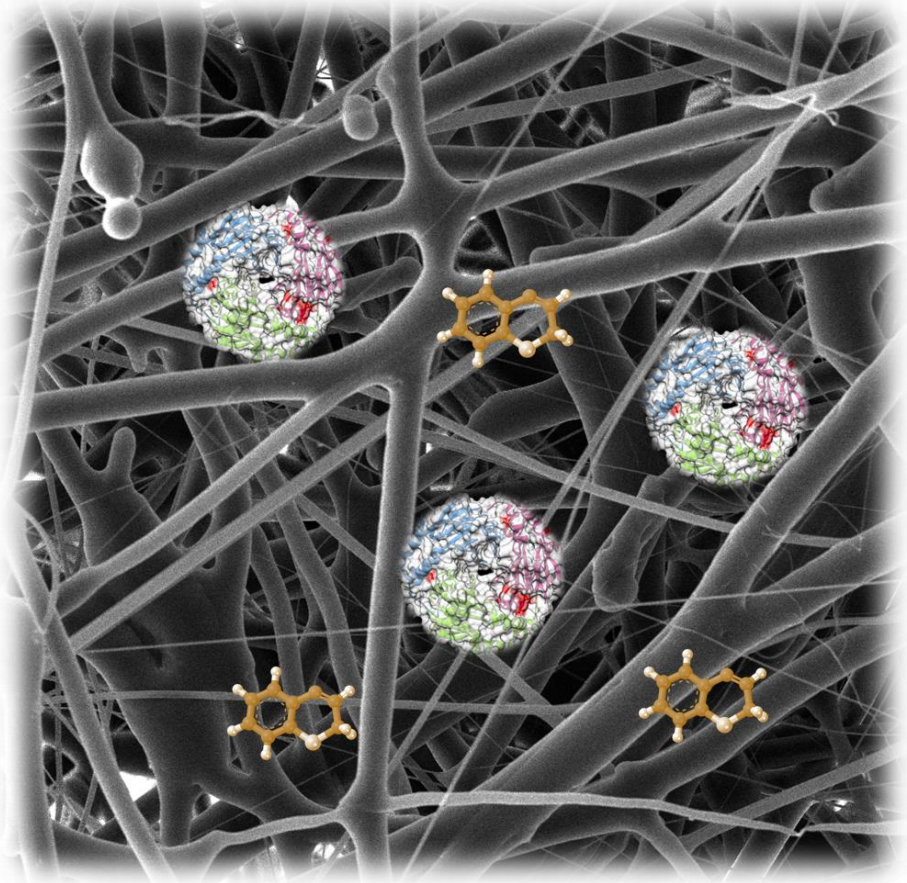


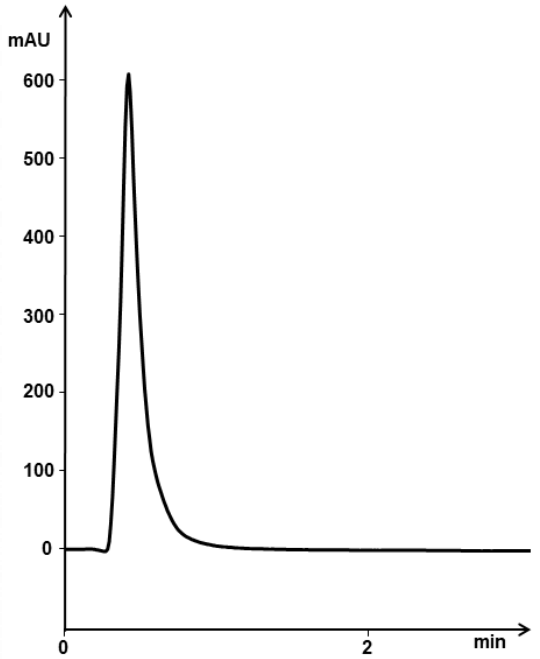
Low molecular weight analytes

- ✓ **Large inter-fiber spaces**
- ✓ **Fiber diameter**



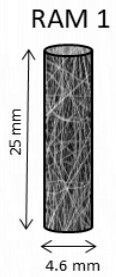
Macromolecular interferences

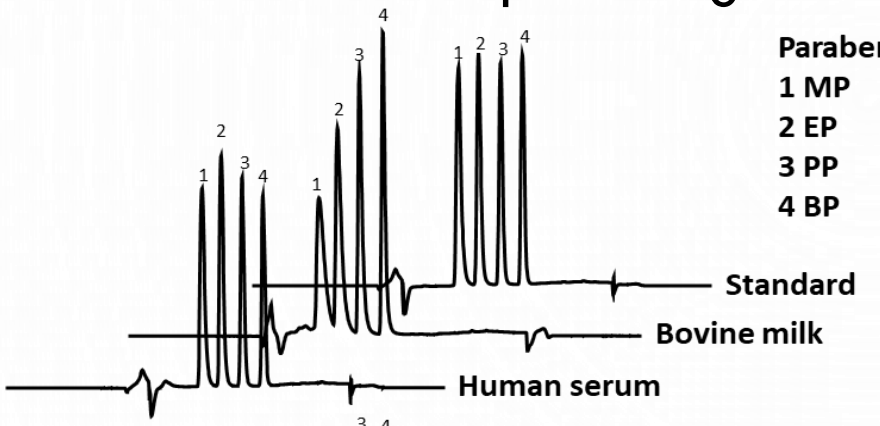


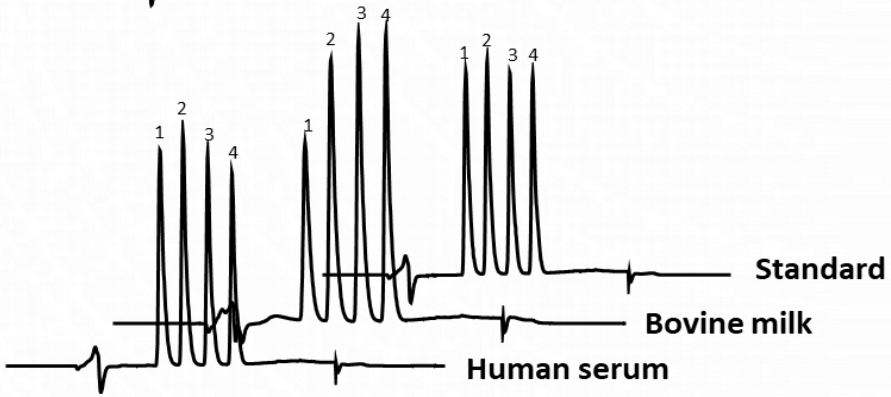


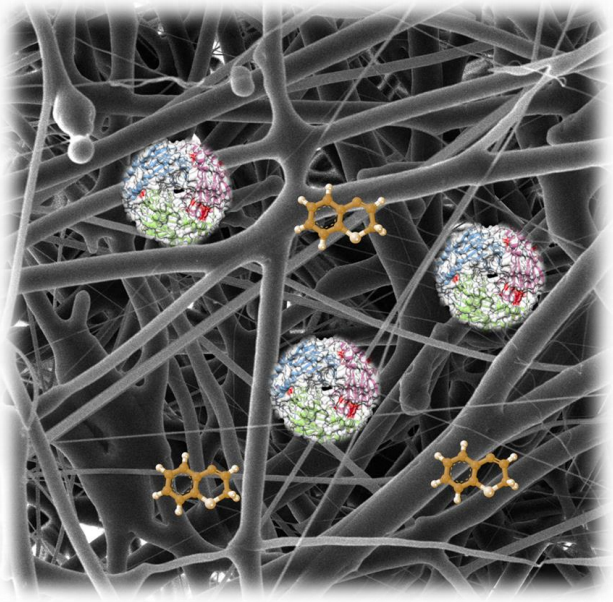
Elution profile of a 10 µL BSA solution using PCL cartridge directly attached to the UV detector

Nanofibers as promising alternative to conventional RAM sorbents

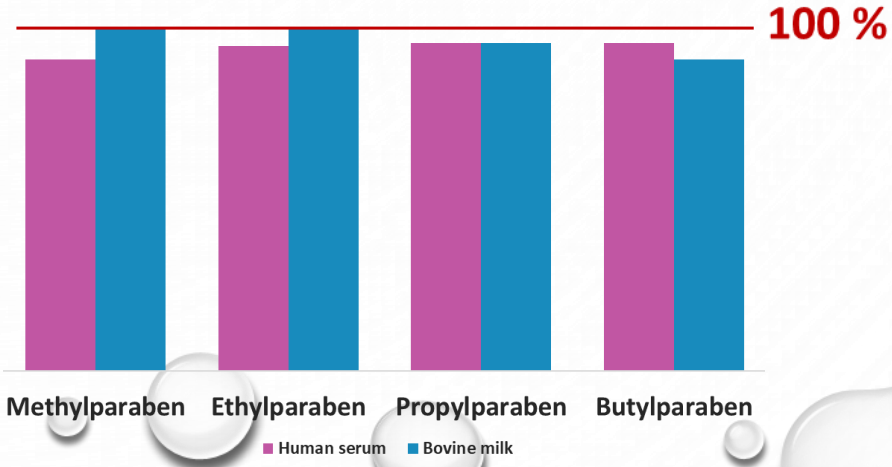






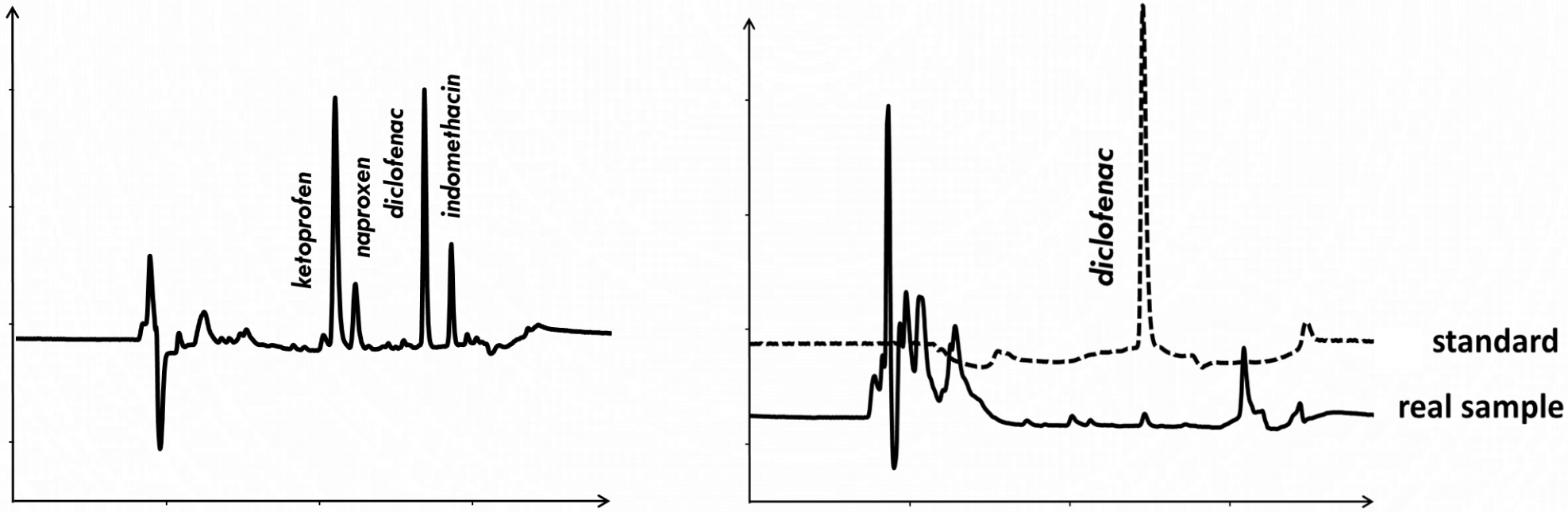


Extraction efficiency [%]

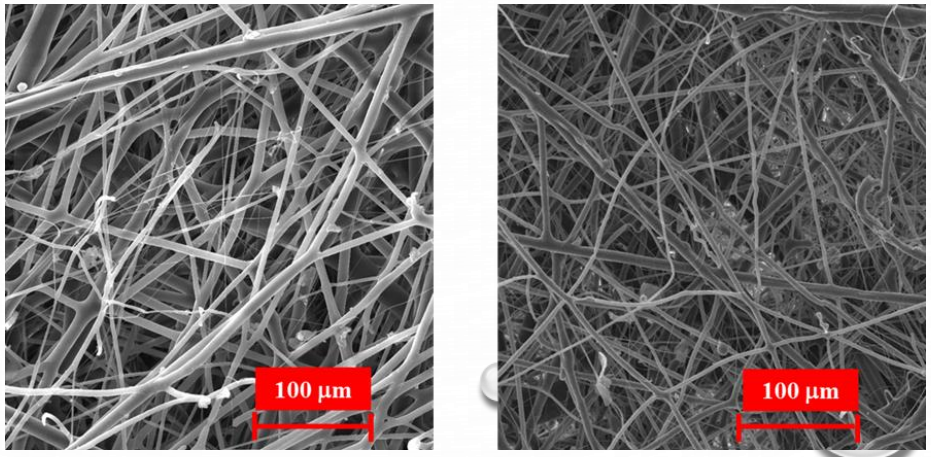


Nanofibers as promising alternative to conventional RAM sorbents

Nanofibers for direct on-line SPE HPLC determination of NSAID in human serum



BEFORE



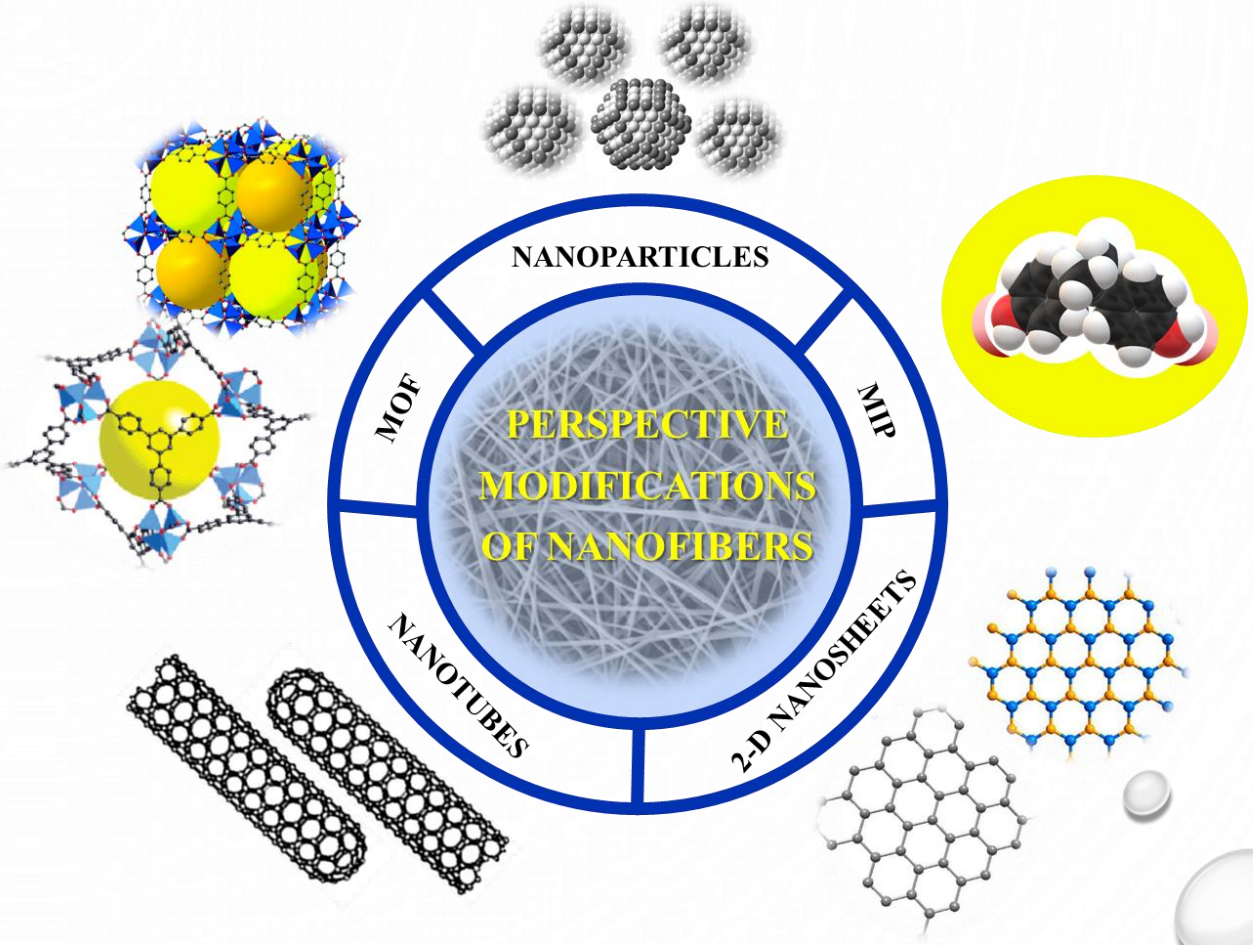
AFTER

The morphology of micro/nanofibrous PCL material before and after **100 injections** of **serum samples**

NO SORBENT DESTRUCTION !

CONCLUSION AND FUTURE TRENDS

- Structural innovations of nanofibers
- New composite and modified polymers
- Graphene-coated nanofibers
- Combination with 3-D printing technology
- Combination of nanofibers with nanotubes and nanoparticles

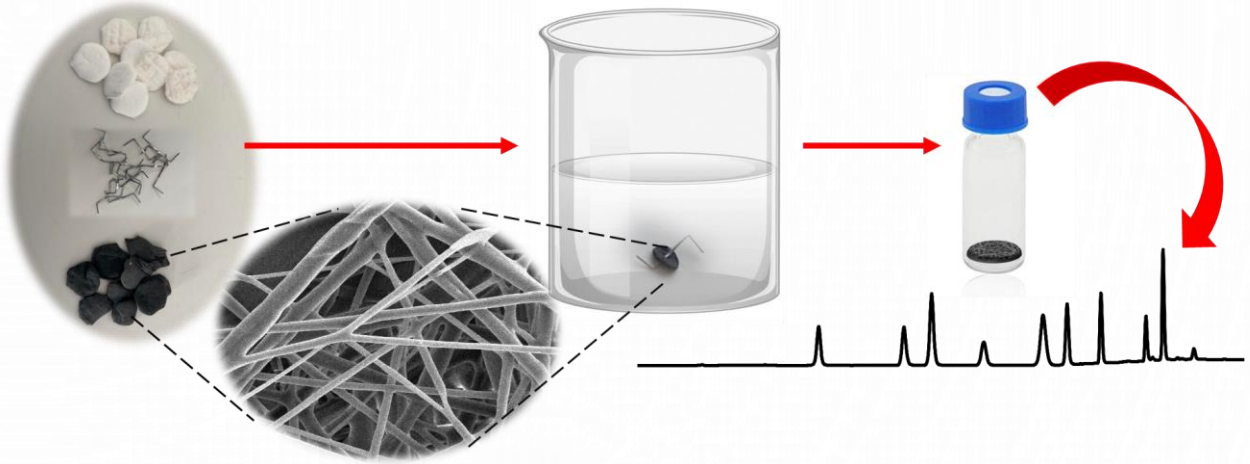


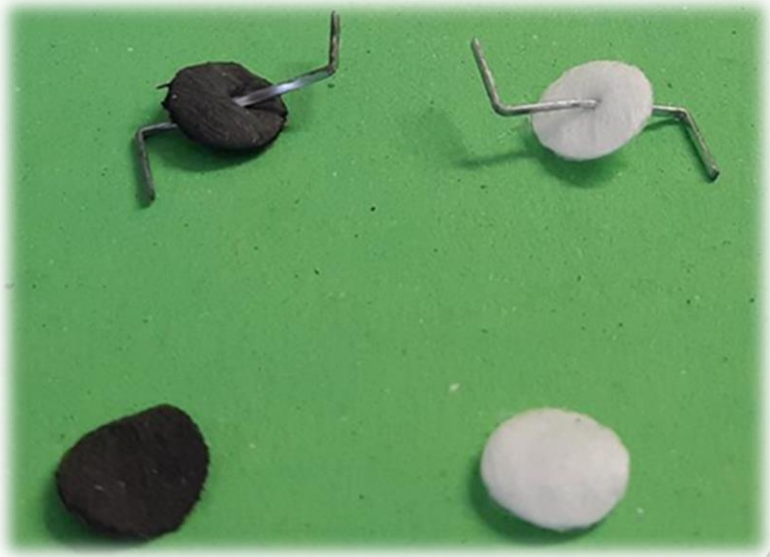
CONCLUSION AND FUTURE TRENDS

- **Centrifugation spin disks**

CONCLUSION AND FUTURE TRENDS

- **Direct „in-vial“ extraction/elution**





THANK YOU FOR YOUR ATTENTION

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(Ing. J. Chvojka, Ing. J. Erben)

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