

Advances in on-line separation in flow injection analysis based on the use of polymer inclusion membranes

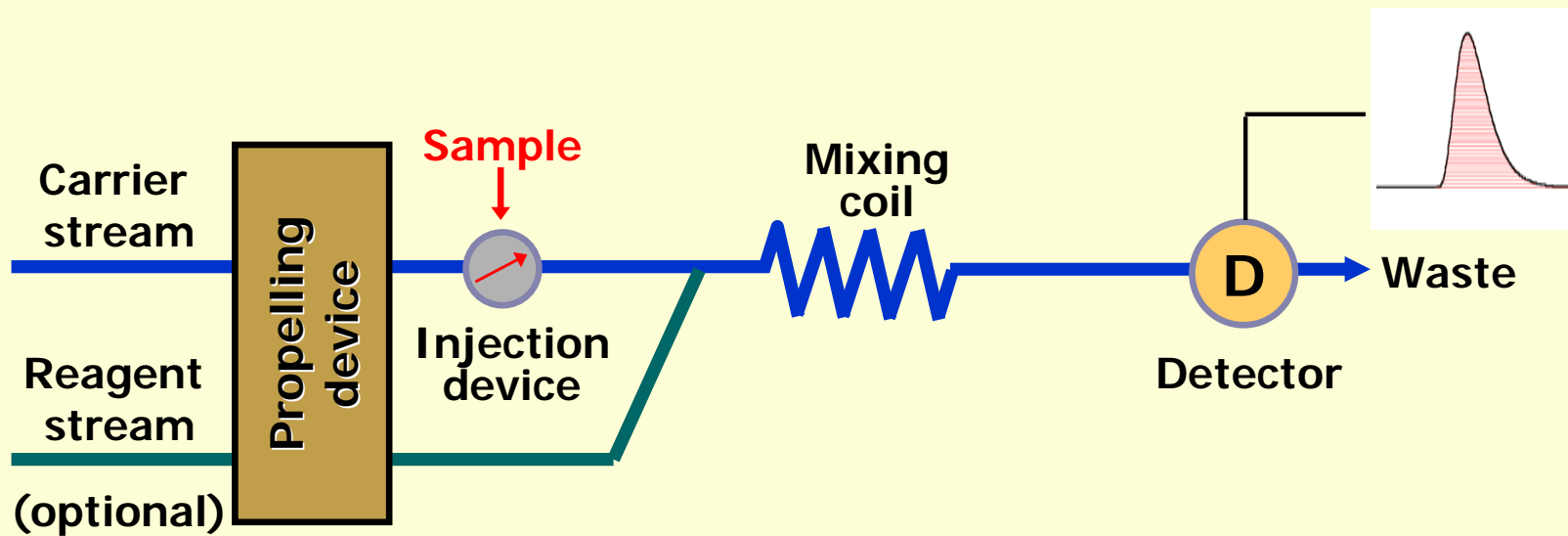
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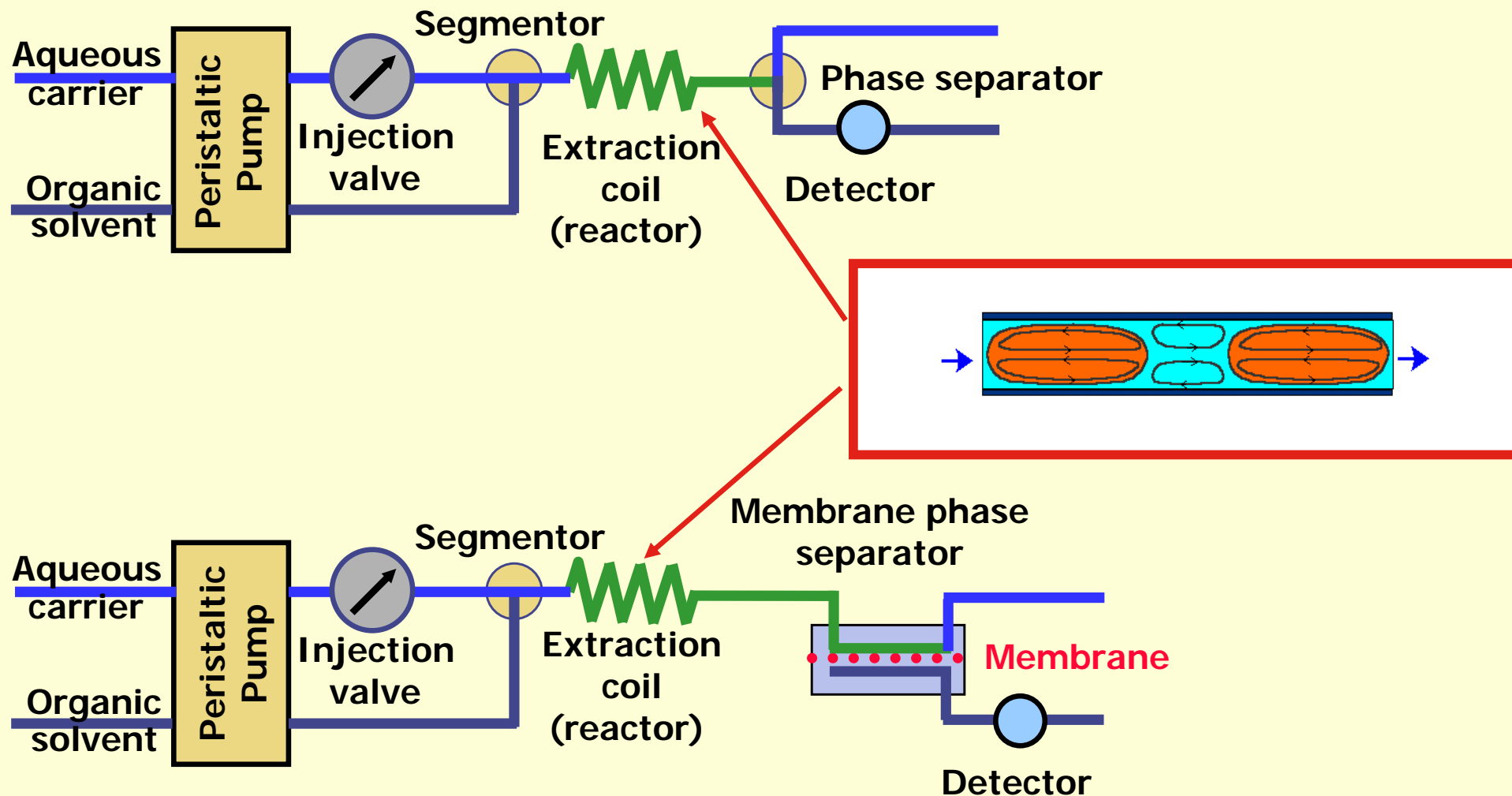
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Flow Injection Analysis



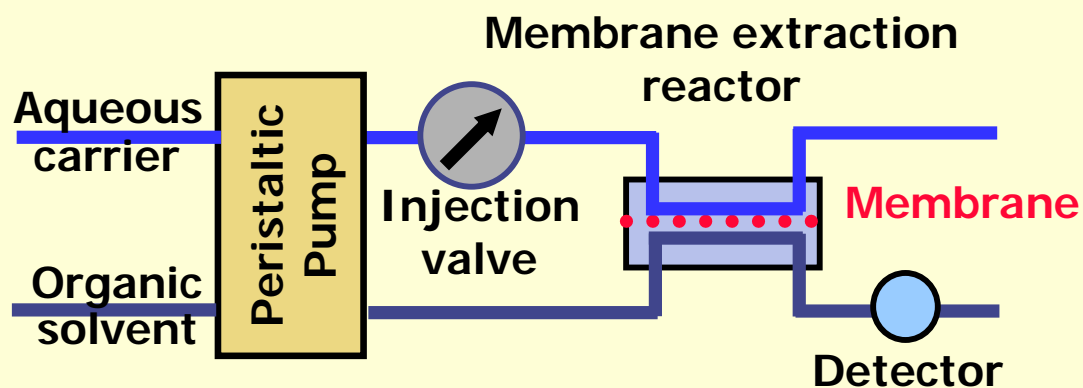
Liquid-liquid Extraction in Flow Injection Analysis


Segmented liquid/liquid extraction




Liquid-liquid Extraction in Flow Injection Analysis


Unsegmented liquid/liquid extraction (Microporous Membrane Liquid-Liquid Extraction - MMLLE)





Solvent Extraction vs Liquid Membrane Extraction

- **Membrane extraction – main advantages**
 - Small amount of solvents
 - High selectivity
 - High flexibility
 - High enrichment factors
 - Integration of the extraction and back-extraction steps
 - **Types of liquid membranes**
 - Bulk liquid membranes (BLMs)
 - Emulsion liquid membranes (ELMs)
 - Supported liquid membranes (SLMs)
 - Polymer inclusion membranes (PIMs)
- 



Supported Liquid Membranes

Structure:

Porous hydrophobic membrane (*e.g.* polytetrafluoroethylene, PTFE; polyvinylidene fluoride, PVDF; polypropylene) **impregnated with a suitable organic liquid containing the extractant.**

Advantages:

- (i) Simple structure;**
- (ii) Easy to use and to integrate the extraction and back-extraction steps.**

Disadvantages:

Limited lifetime because of slow leaching of the membrane liquid phase into the adjacent solutions



Polymer Inclusion Membranes

Composition:

- **Base polymer** (*e.g.* PVC, cellulose triacetate)
- **Extractant** (*e.g.* Cyanex 301/302/272, Aliquat 336, Alamine 336, di(2-ethylhexyl)phosphoric acid (D2EHPA))
- **Plasticizer/modifier** (*e.g.* 2-nitrophenyloctylether, dioctylphthalate, *n*-decanol)

Physical characteristics

- Homogeneous
- Transparent
- Flexible and mechanically strong

Advantages: Longer lifetime than supported liquid membranes due to the reduced loss of the membrane liquid phase.

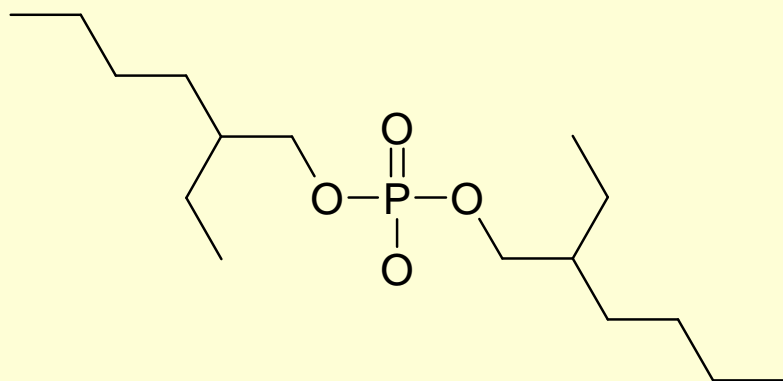
Membrane Preparation

PIM composition:

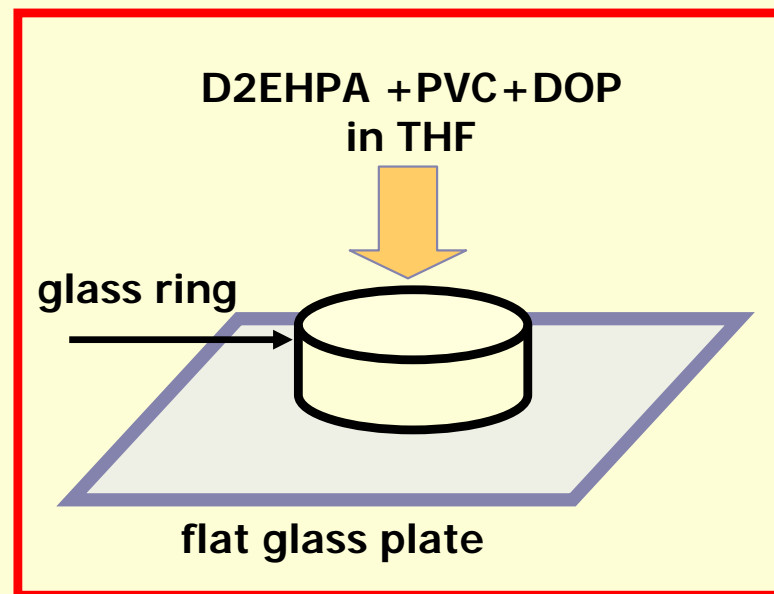
50% PVC

40% D2EHPA

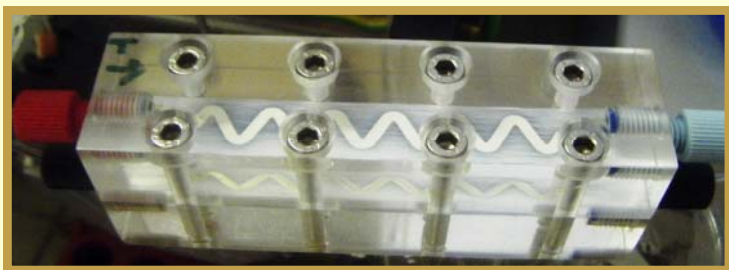
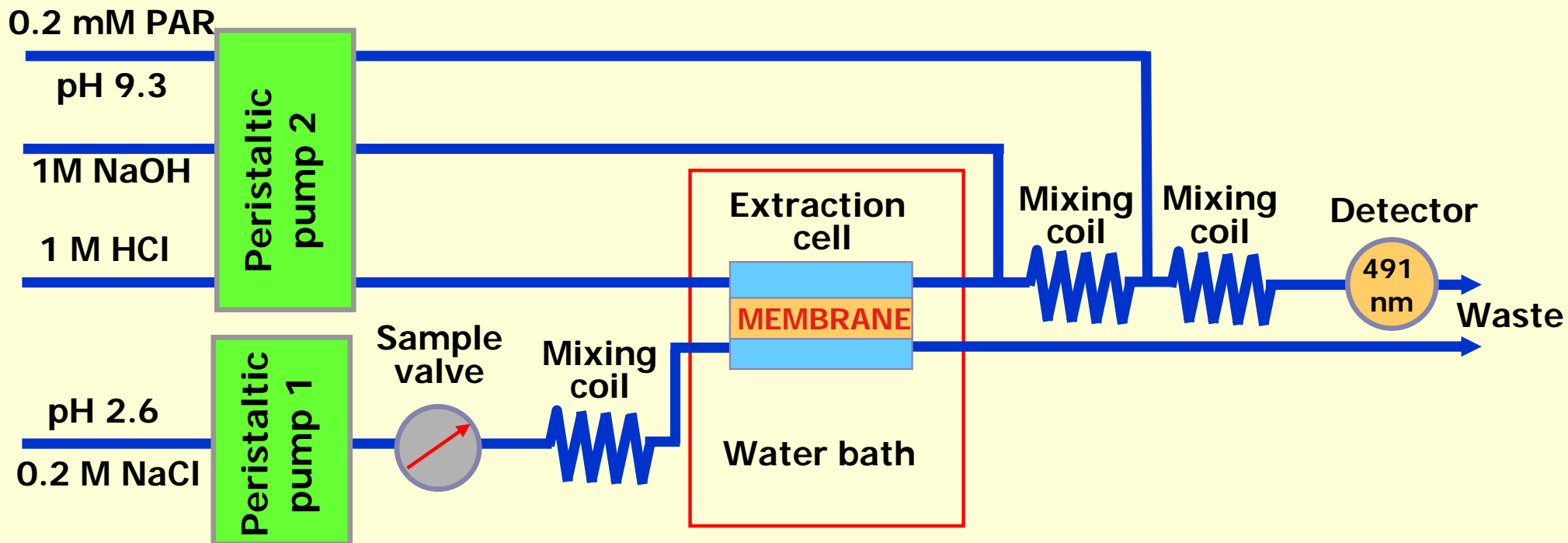
(di-2-ethylhexyl phosphoric acid)



10% DOP (dioctylphthalate)

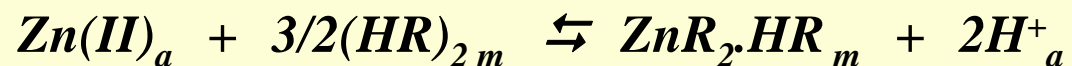


Flow Injection System

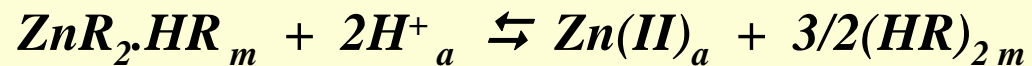


Extraction cell

Donor stream:



Acceptor solution:





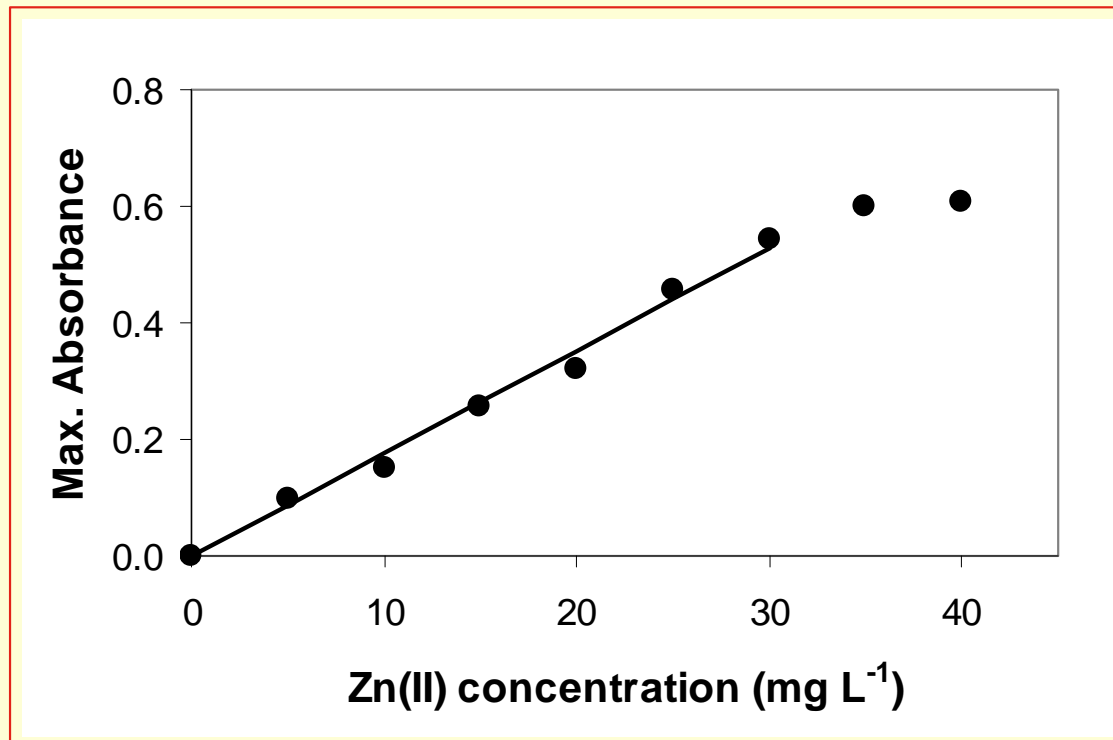
Optimization of the Flow Injection System

- **Acceptor stream:**
stop-time (5 min)
flow rate (0.85 mL min^{-1}) after the stop-time
- **Donor stream:**
pH (2.6)
flow rate (0.30 mL min^{-1})
- **Reconditioning of the membrane: (10 min)**

Calibration of the Flow Injection System

Analytical Figures of Merit

Sampling rate (h^{-1})	4
Detection limit (mg L^{-1})	0.05
RSD (%)	3.4
Linear range (mg L^{-1})	up to 30



Analysis of Real Samples

Pharmaceutical samples	Zn(II) conc. (mg L⁻¹)	
	FIA	AAS
ZnSO ₄	6.76±0.13	7.45±0.05
Amino acid chelated Zn(II)	19.6±0.80	19.0±0.1
Galvanizing samples	Zn(II) conc. (g L⁻¹)	
	FIA	AAS
1	67.1±0.7	67.8±0.3
2	53.9±1.2	53.7±0.2
3	110±3	115±0.3
4	54.7±0.7	56.4±0.4



Conclusions

The use of Polymer Inclusion Membranes in Flow Analysis shows a considerable promise for the selective separation and pre-concentration of analytes prior to their analytical measurement.

