Determination of the Composition of Natural Rosins using Cyclodextrin-modified Capillary Electrophoresis

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IRCSET Enterprise Partnership Scheme

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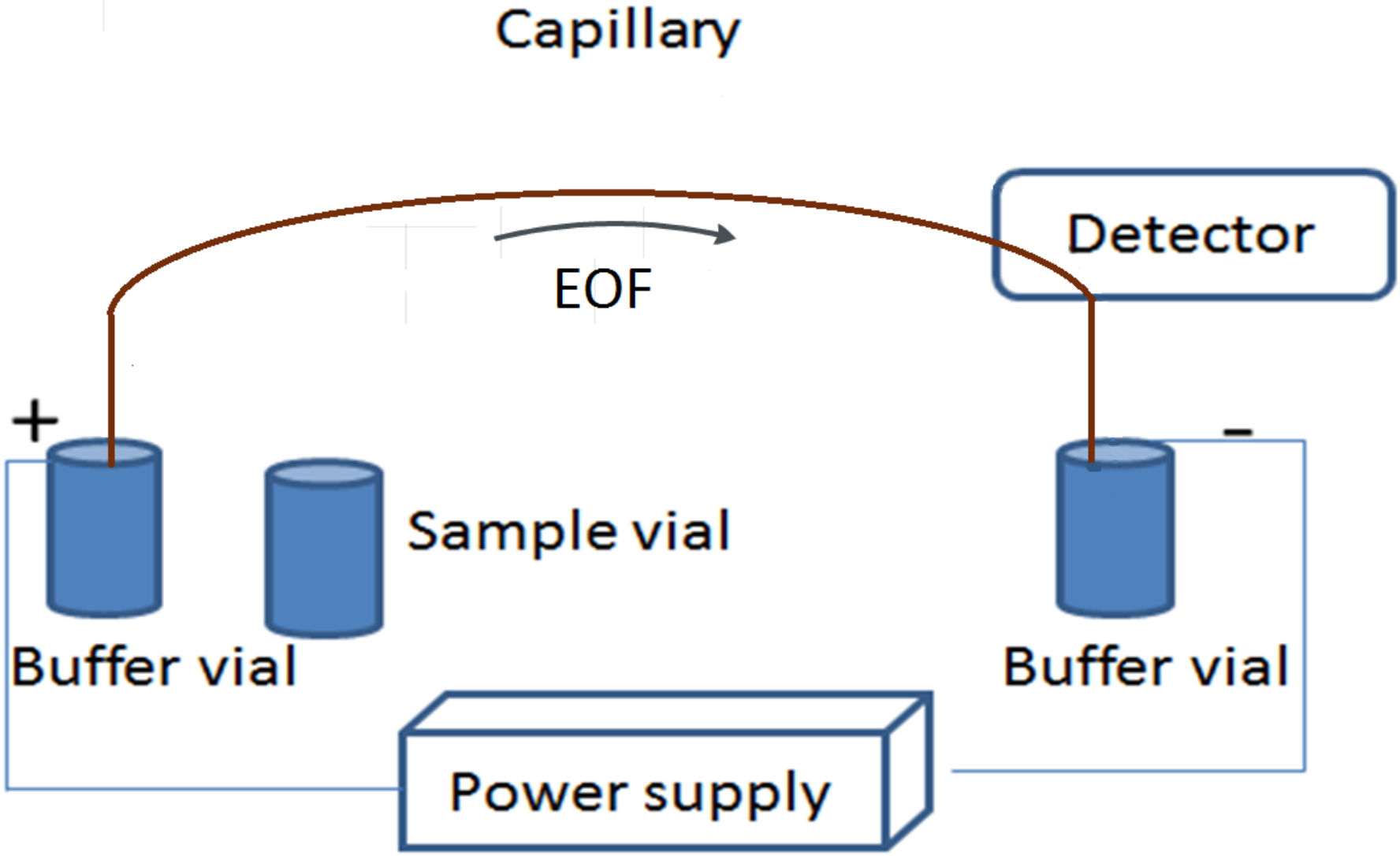
Outline

- Aims of the project
- Capillary electrophoresis
- Cyclodextrin modified CE
- Acid separation method
- MEKC and MEEKC
- Terpene separation method

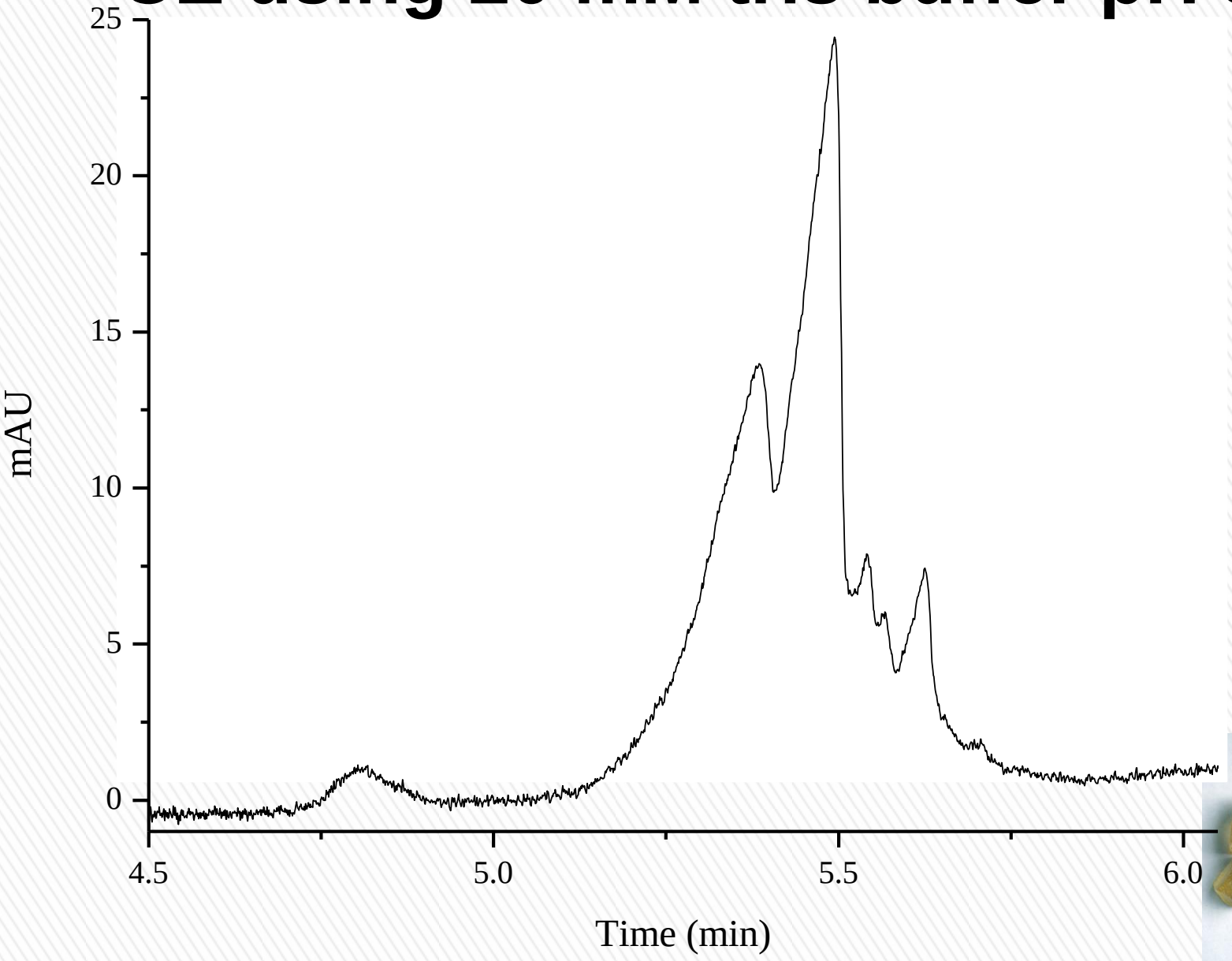
Aims

- Development of a Capillary Electrophoresis (CE) method for rosin analysis
- Determination of chemical composition of rosin samples of different origin.

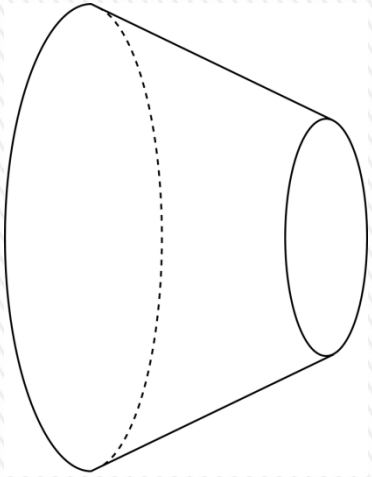
Capillary Electrophoresis



Determination of rosin composition by CE using 20 mM tris buffer pH 8



Cyclodextrins



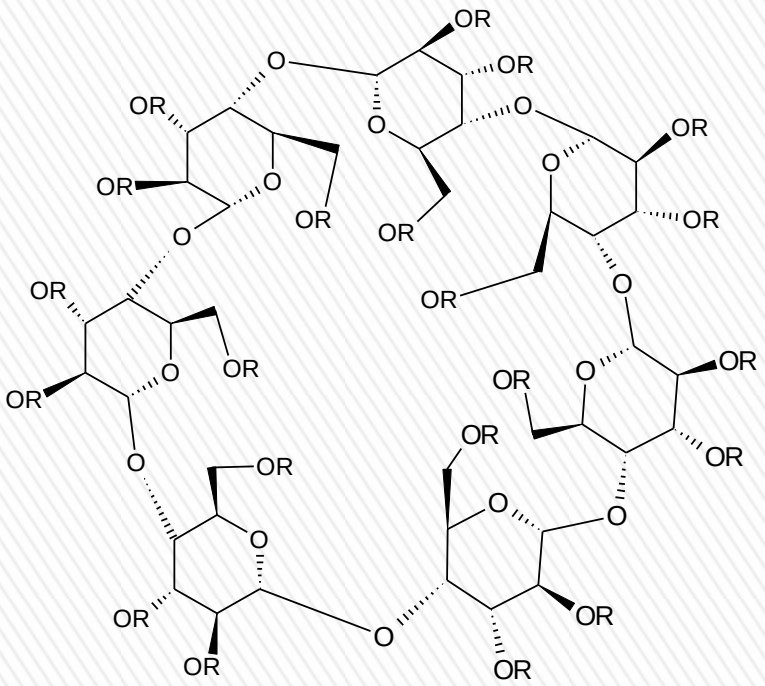
Cyclic oligosaccharides

	α	β	γ
Glucose units	6	7	8
Cavity width (nm)	0.47-0.53	0.6-0.65	0.75-0.83
Cavity depth (nm)	0.79	0.79	0.79

Hydrophobic inner cavity

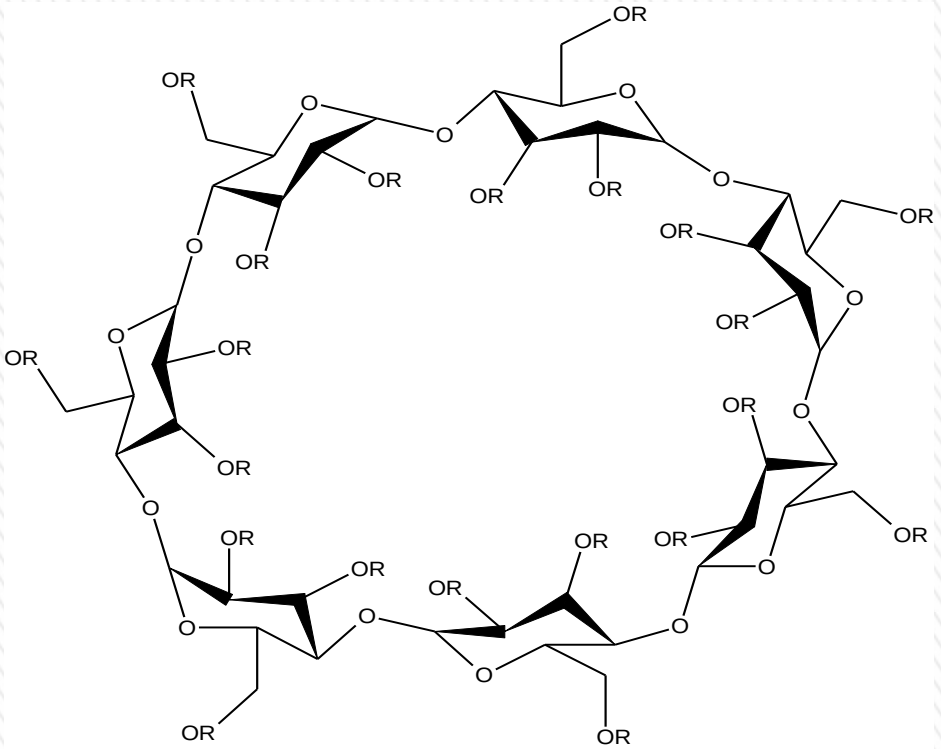
Hydrophilic outer surface

Derivatized Cyclodextrins



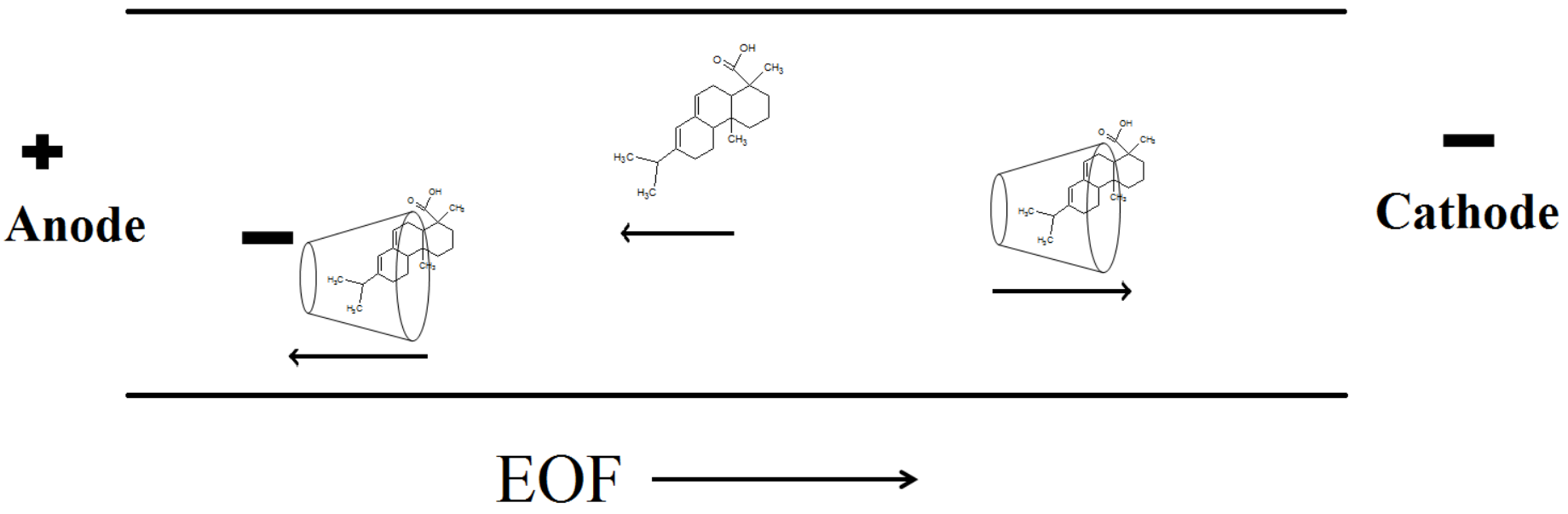
R = H or -CH_3

Methyl-β-cyclodextrin

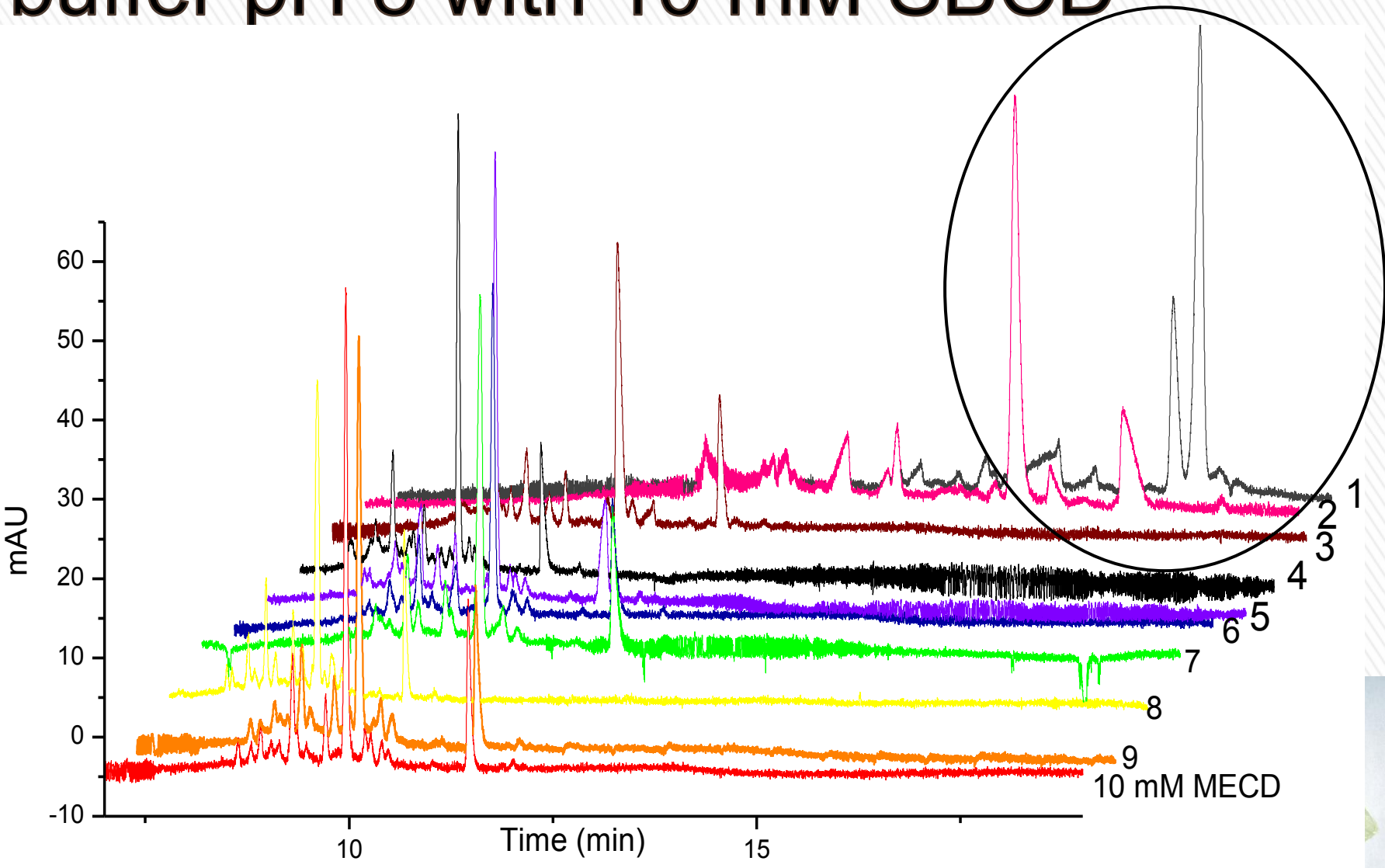


Sulfobutylether-β-cyclodextrin

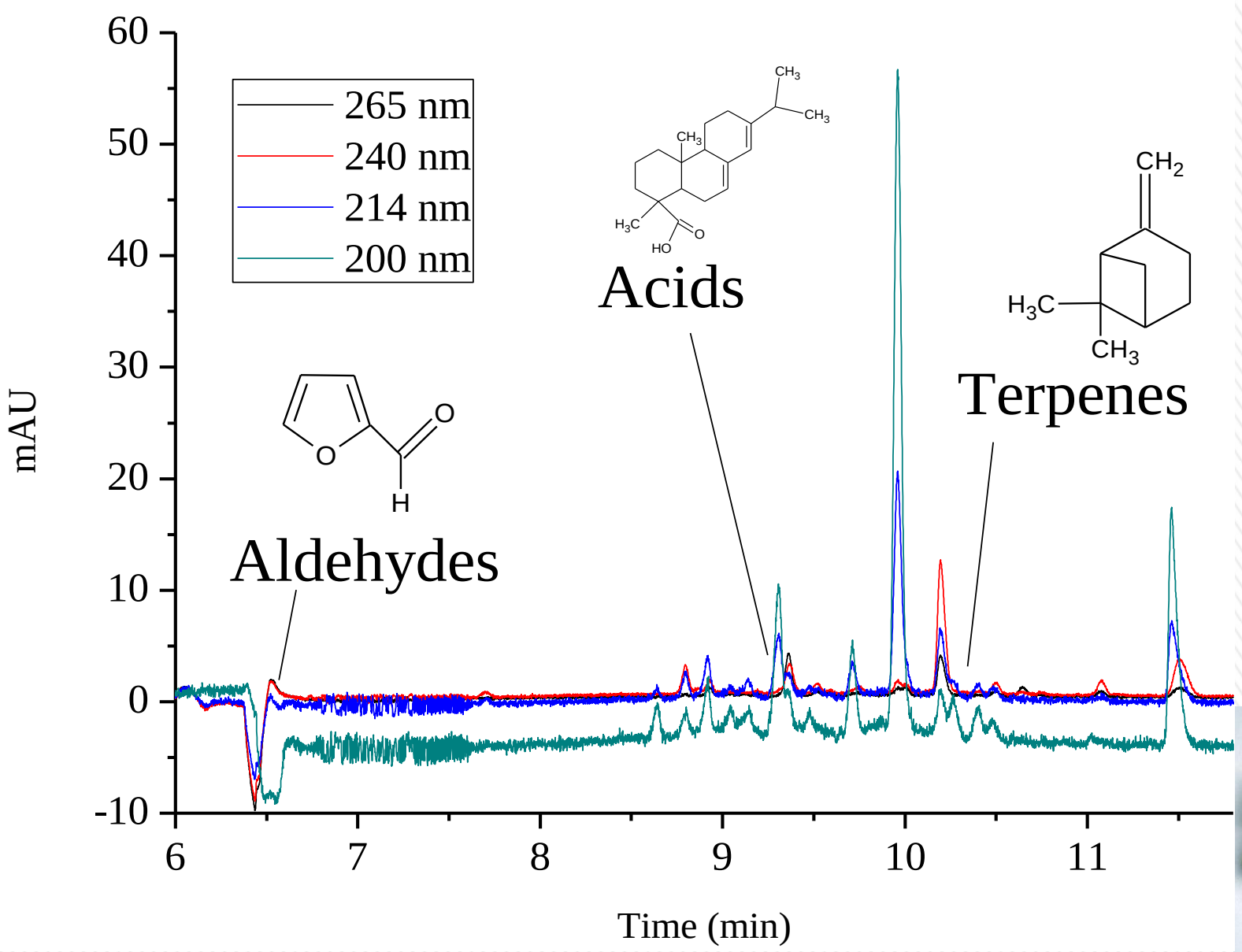
Cyclodextrins in a capillary



Variation of neutral CD in 20 mM tris buffer pH 8 with 10 mM SBCD



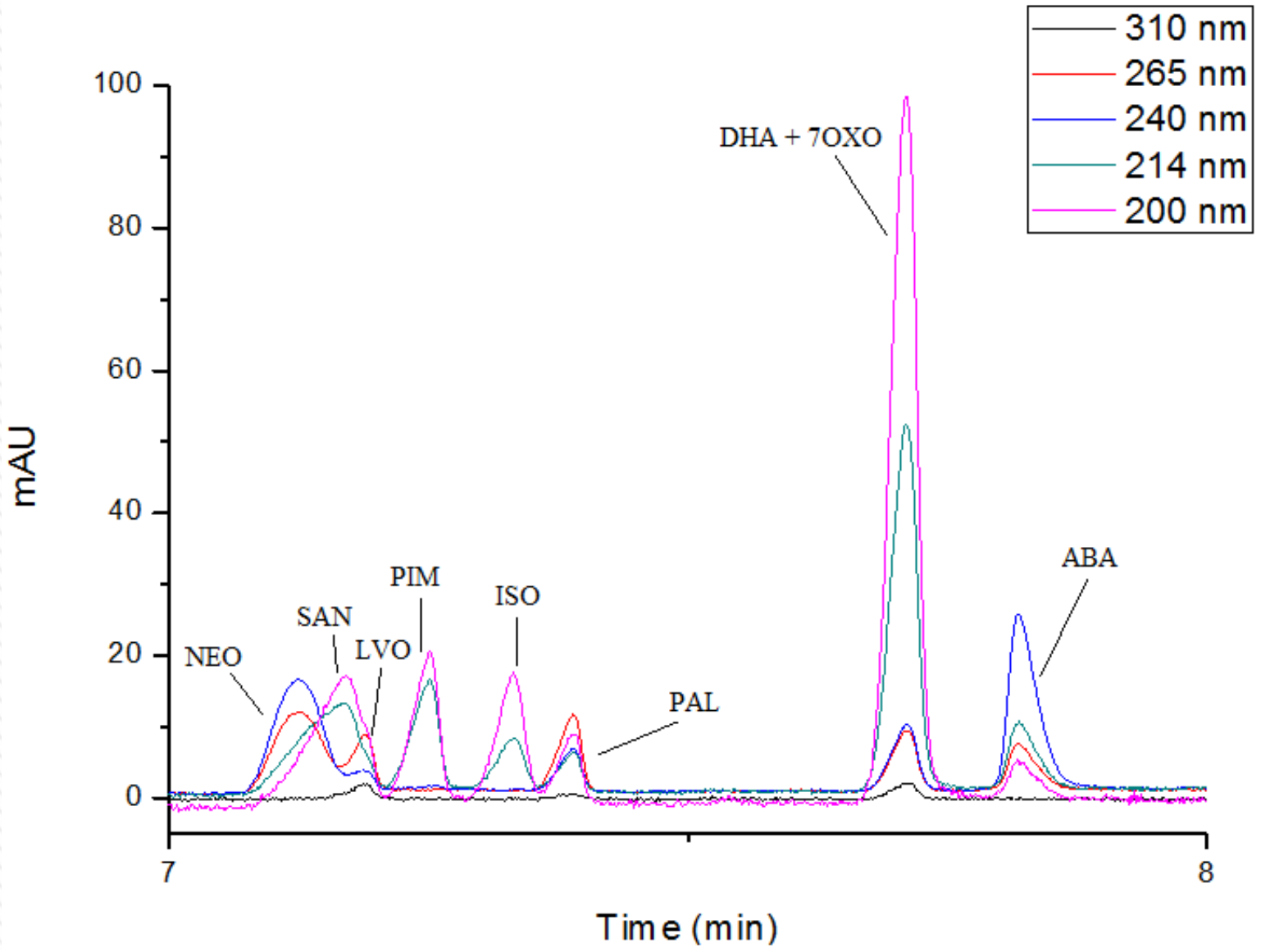
Separation of the three chemical groups



Resin acids

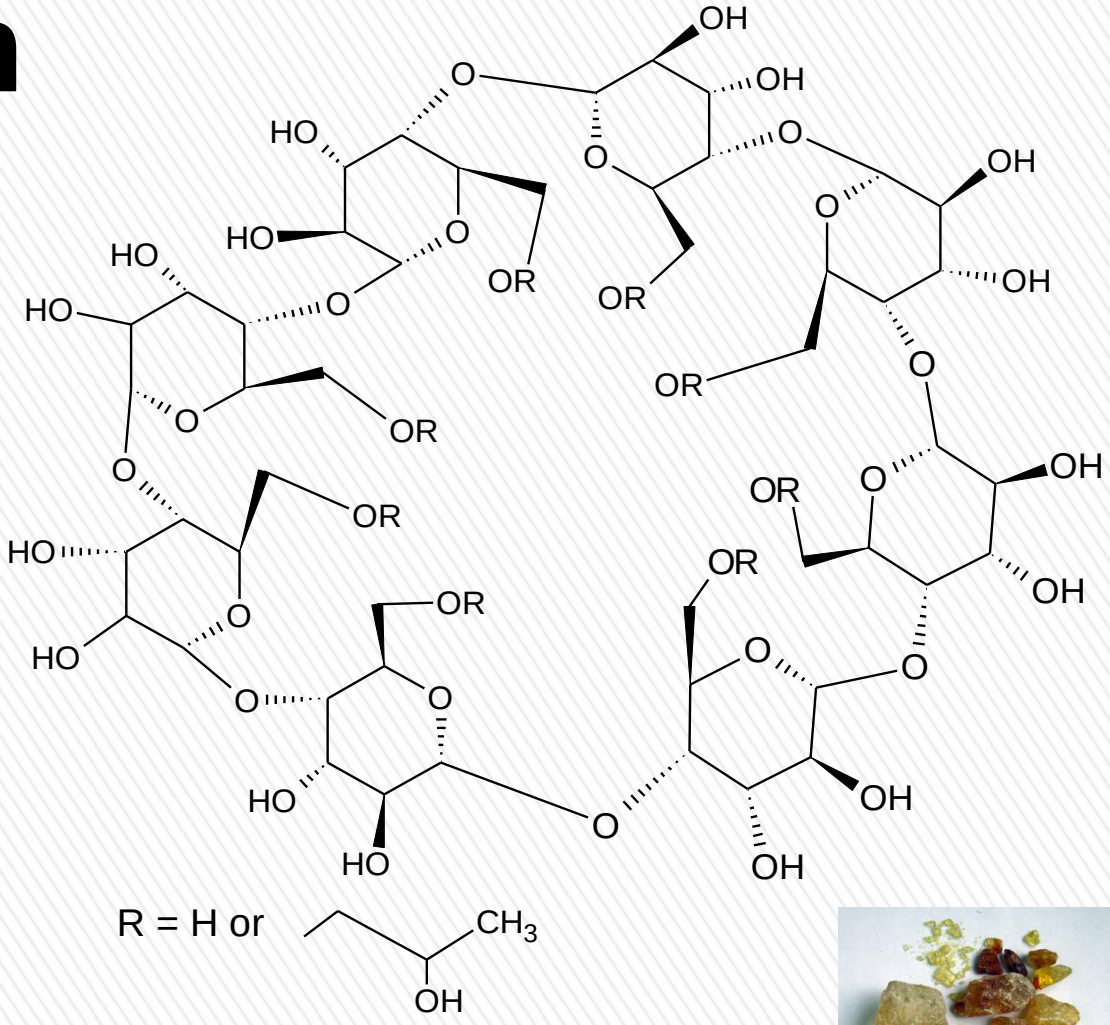
Acid	Abbreviation
Abietic acid	(ABA)
Neoabietic acid	(NEO)
Dehydroabietic acid	(DHA)
7-Oxodehydroabietic acid	(7OXO)
Palustric acid	(PAL)
Levopimaric acid	(LVO)
Pimaric acid	(PIM)
Isopimaric acid	(ISO)
Sandaracopimaric acid	(SAN)

0.01% w/v mixed acid standard in MeOH

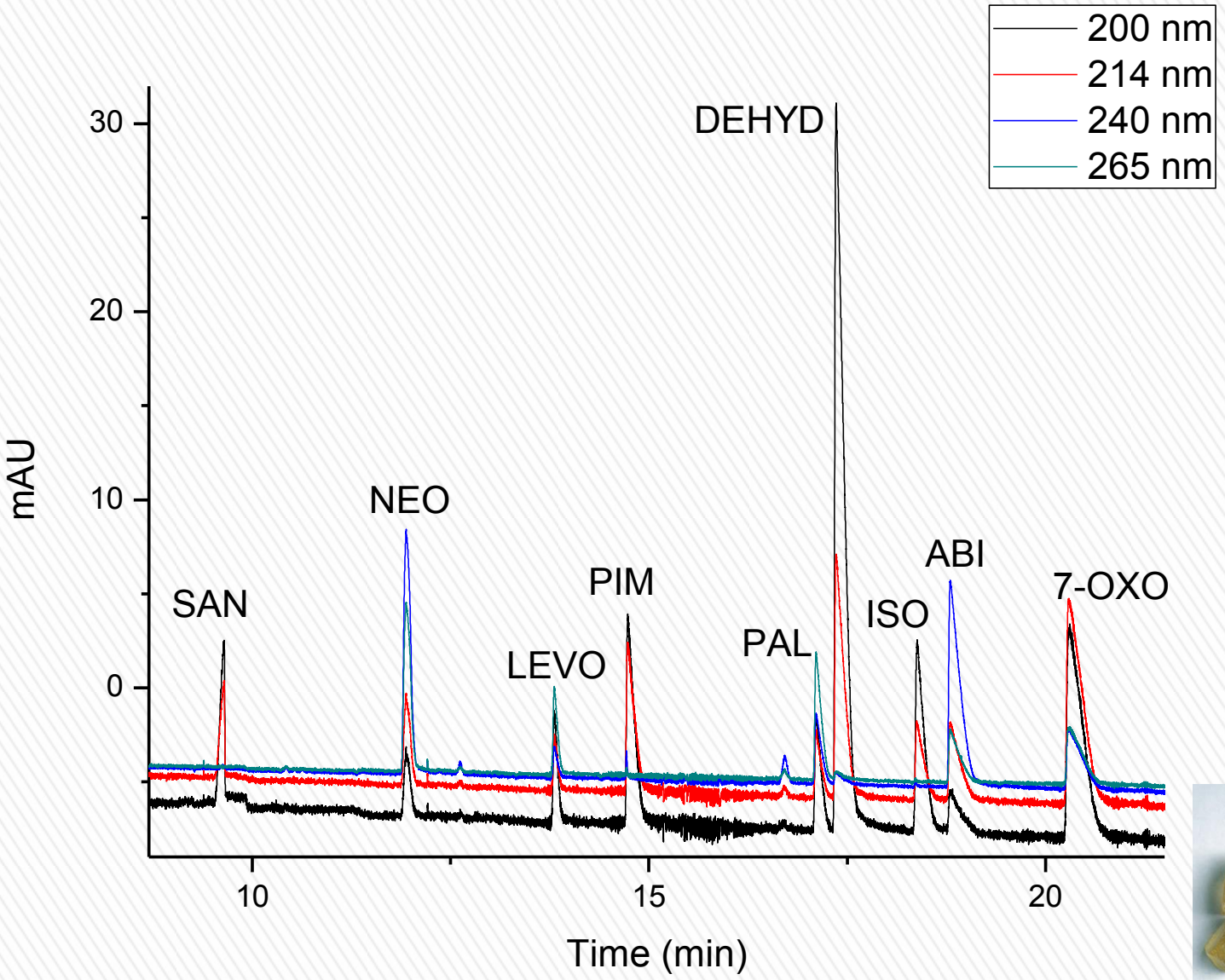


2-hydroxypropyl γ cyclodextrin

- Neutral
- Larger cavity

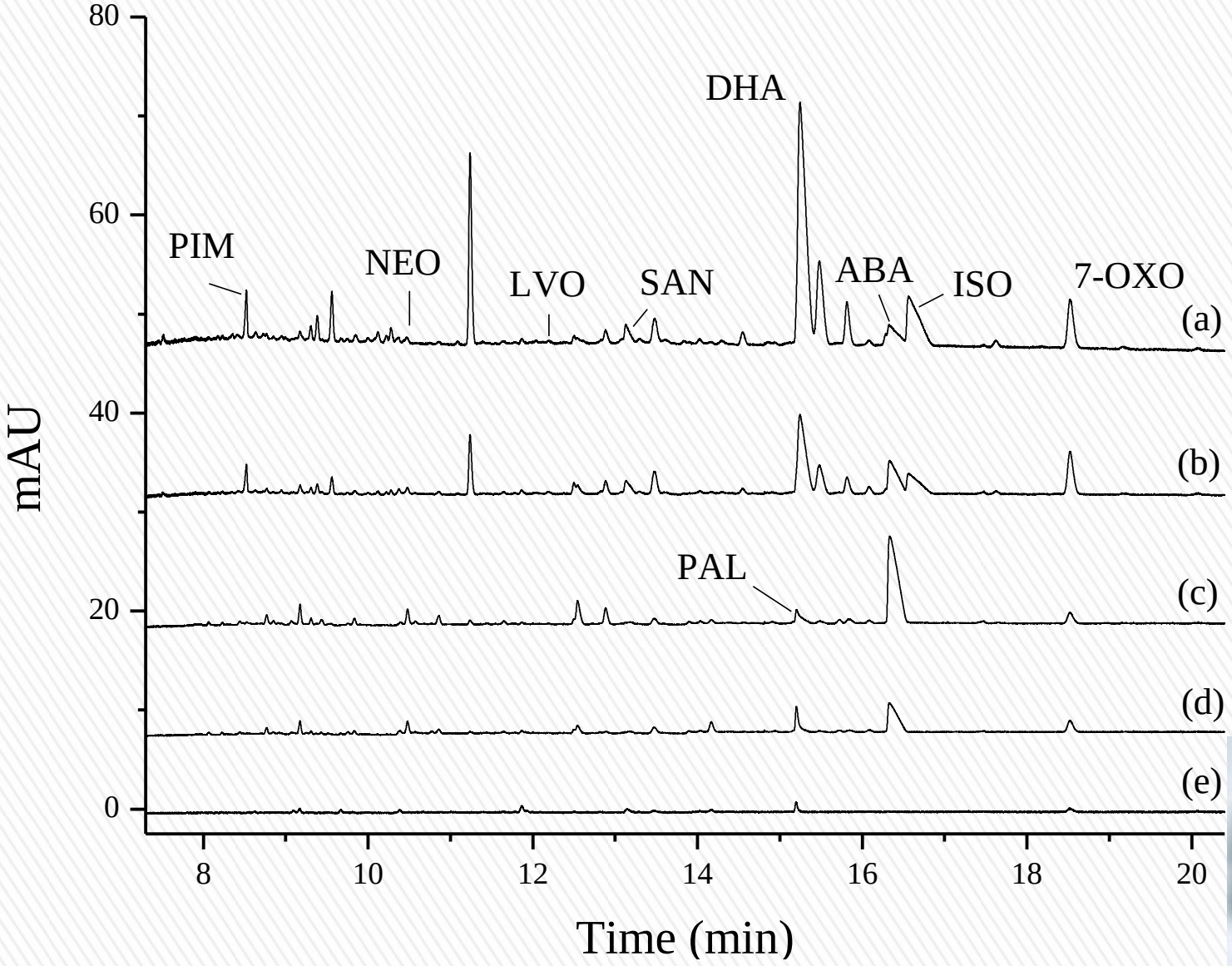


Optimised separation of acid standards



0.01% w/v acid mix in MeOH, 5 mM 2-HPγCD, 10 mM SBCD in 20 mM Tris pH

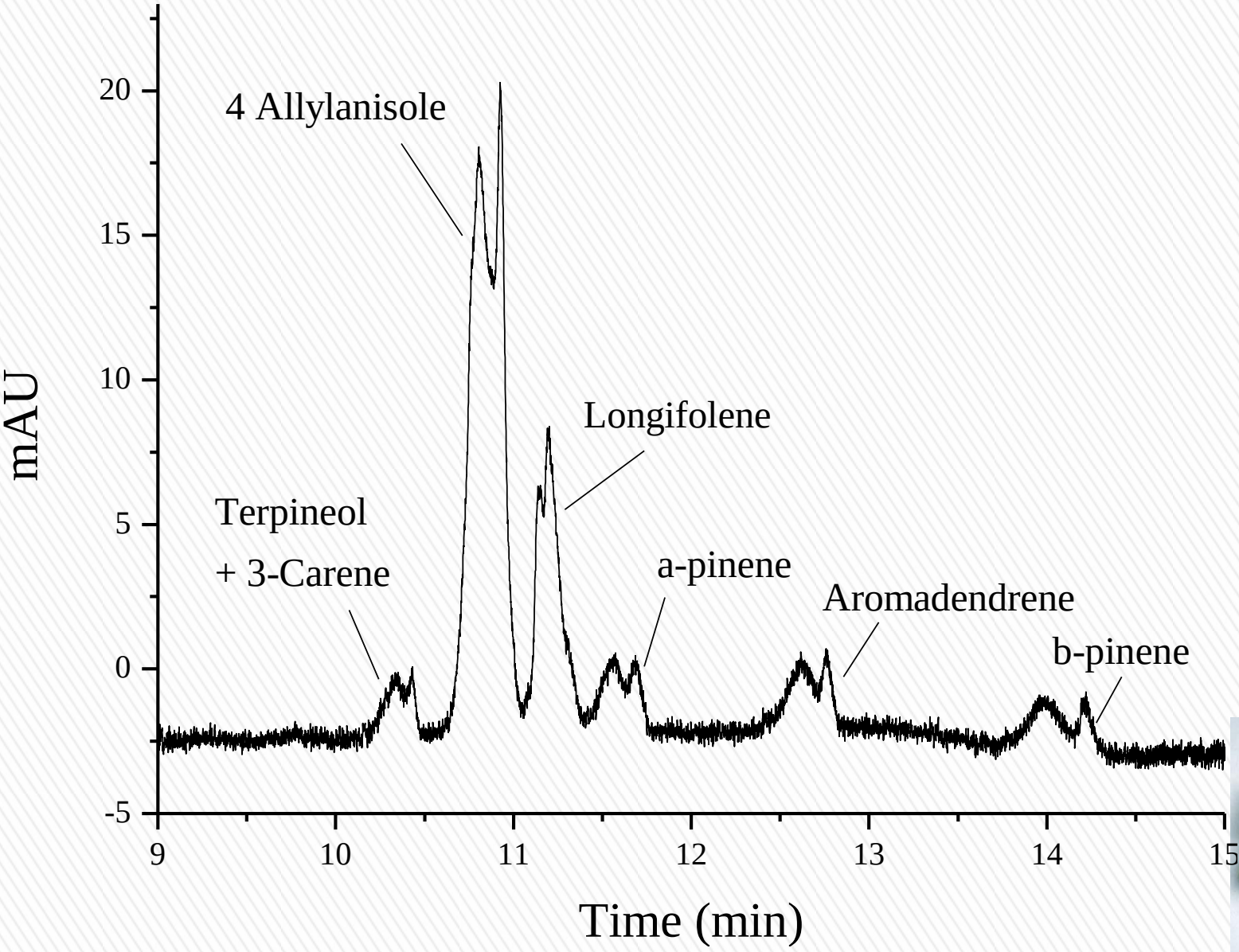
Analysis of 0.1% w/v gum rosin



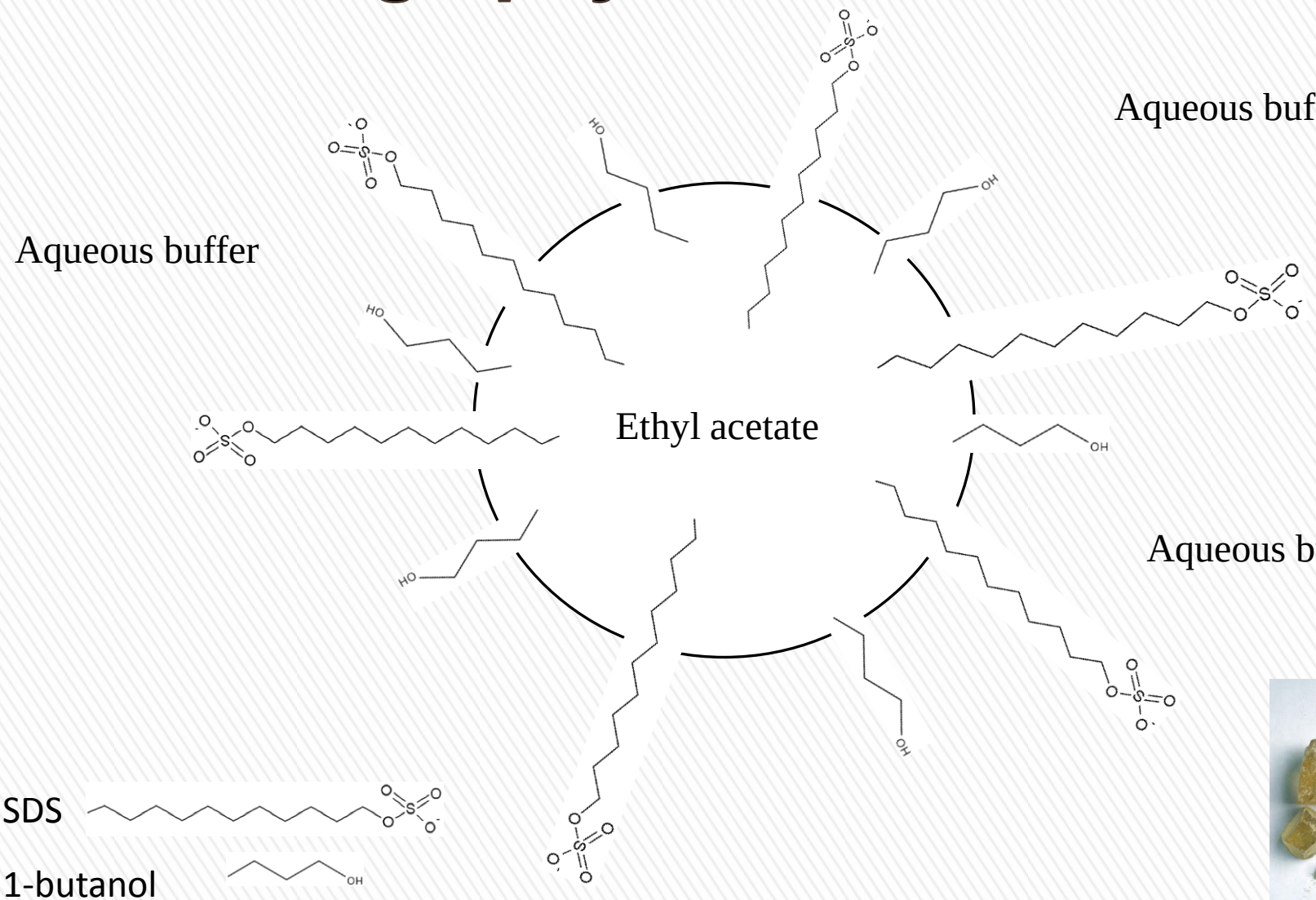
Acid concentrations in gum rosin

Acid	‘Good’ rosin Conc. (mg/L)	‘Bad rosin’ Conc. (mg/L)
ABA	79.5	132.7
7-OXO	9.0	8.4
ISO	65.4	73.7
PIM	29.4	28.9
SAN	16.1	14.8
LVO	3.5	6.8
DHA	49.8	38.9
PAL	22.5	24.9
NEO	11.2	16.2

Initial terpene separation



Microemulsion electrokinetic chromatography



SDS

1-butanol

MEEKC

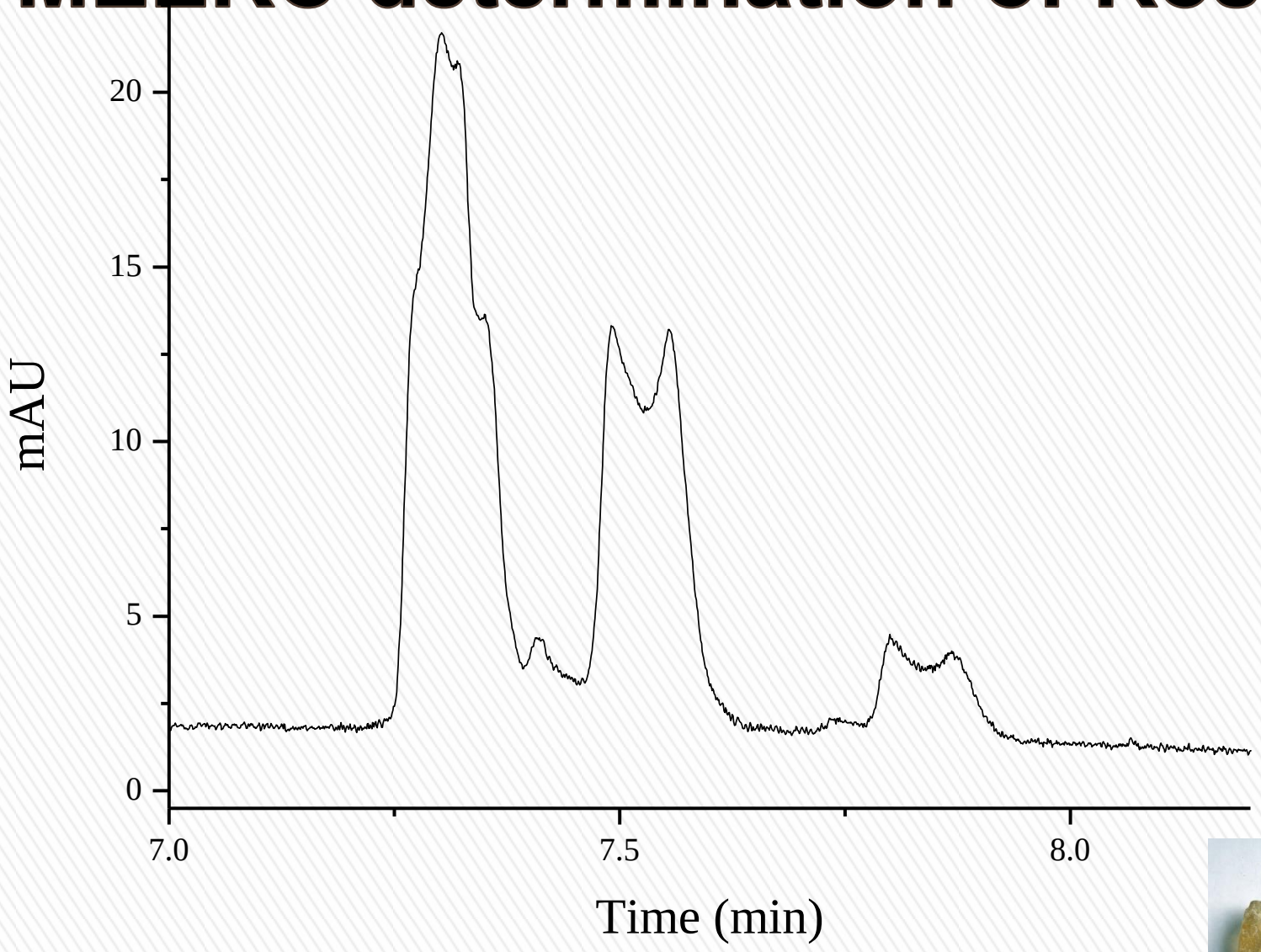
- Usually high pH used
  - Very long migration times
  - Bad reproducibility
- pH 2 $\longrightarrow$ no EOF

- Mobility of the microemulsions towards anode
- Reverse polarity

MEEKC optimisation

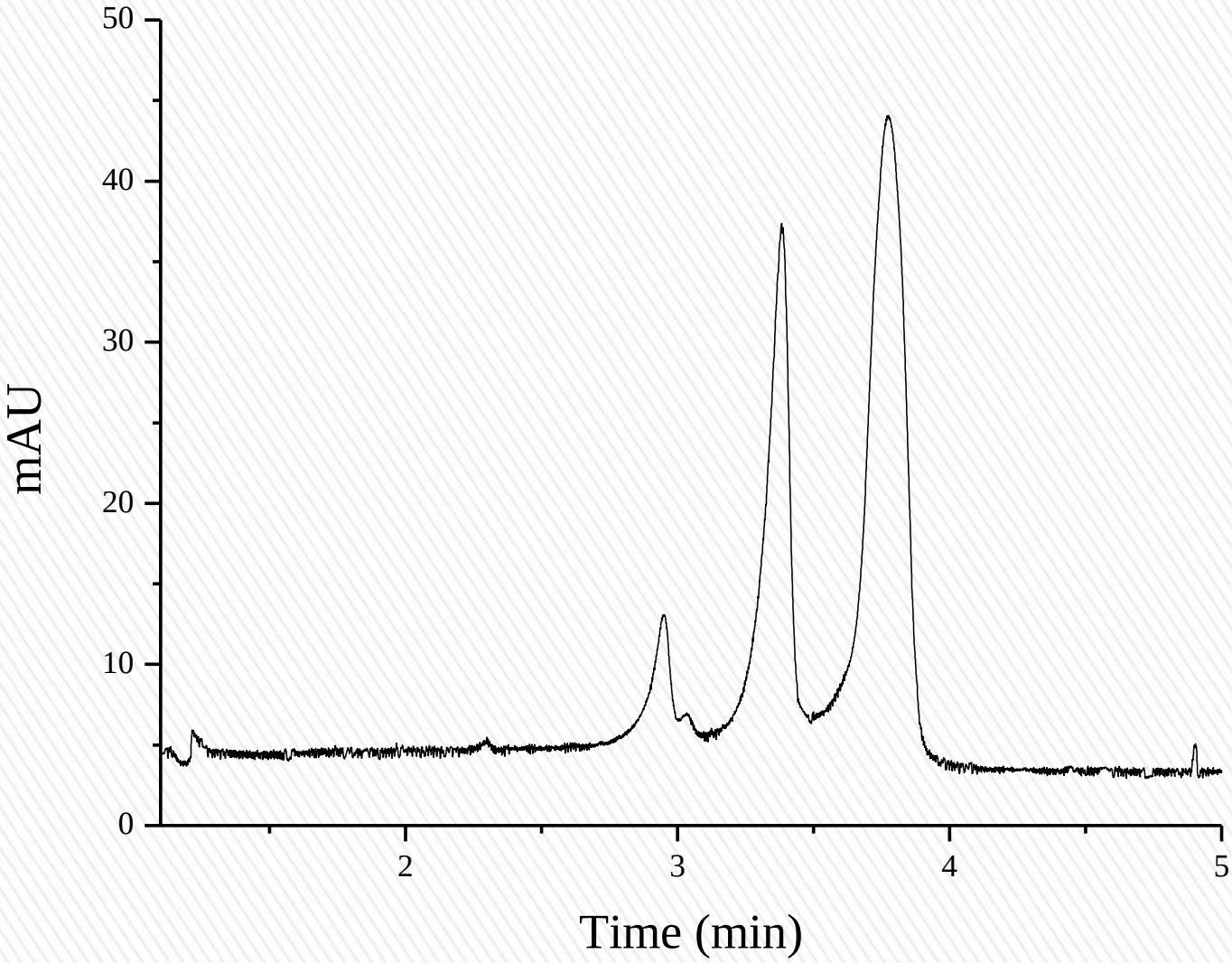
- **Buffer**
  - 10 mM phosphate pH 2
- **Oil type**
  - Ethyl acetate
- **Ethyl acetate**
  - 1%
- **1-butanol**
  - 6%
- **SDS**
  - 4%

MEEKC determination of Rosin

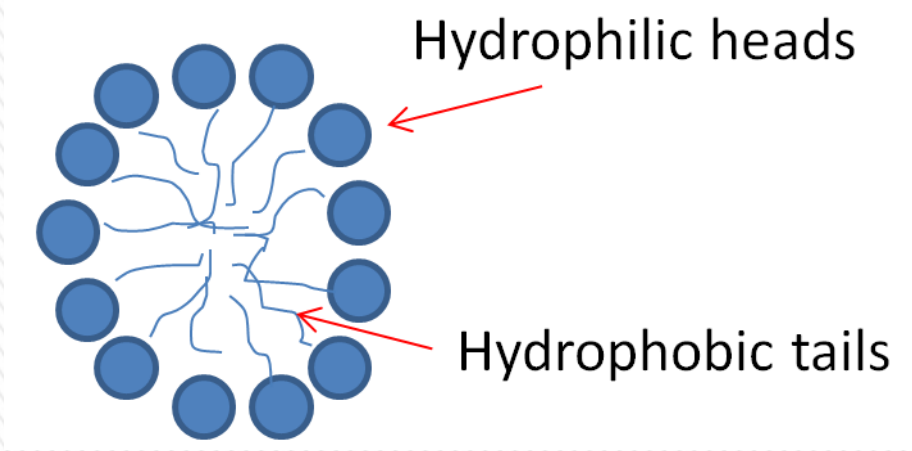


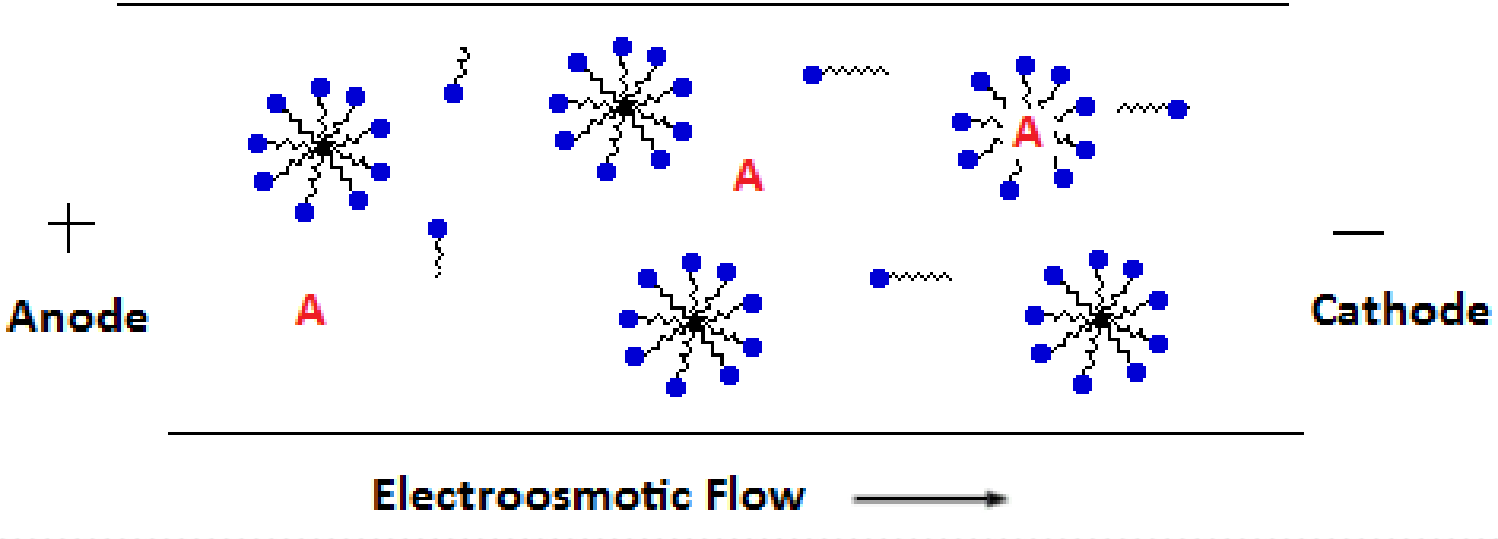
6% 1-butanol, 4% SDS, 1% ethyl acetate, 10mM phosphate pH 2

Short end injection – 10 mM tris buffer pH 8



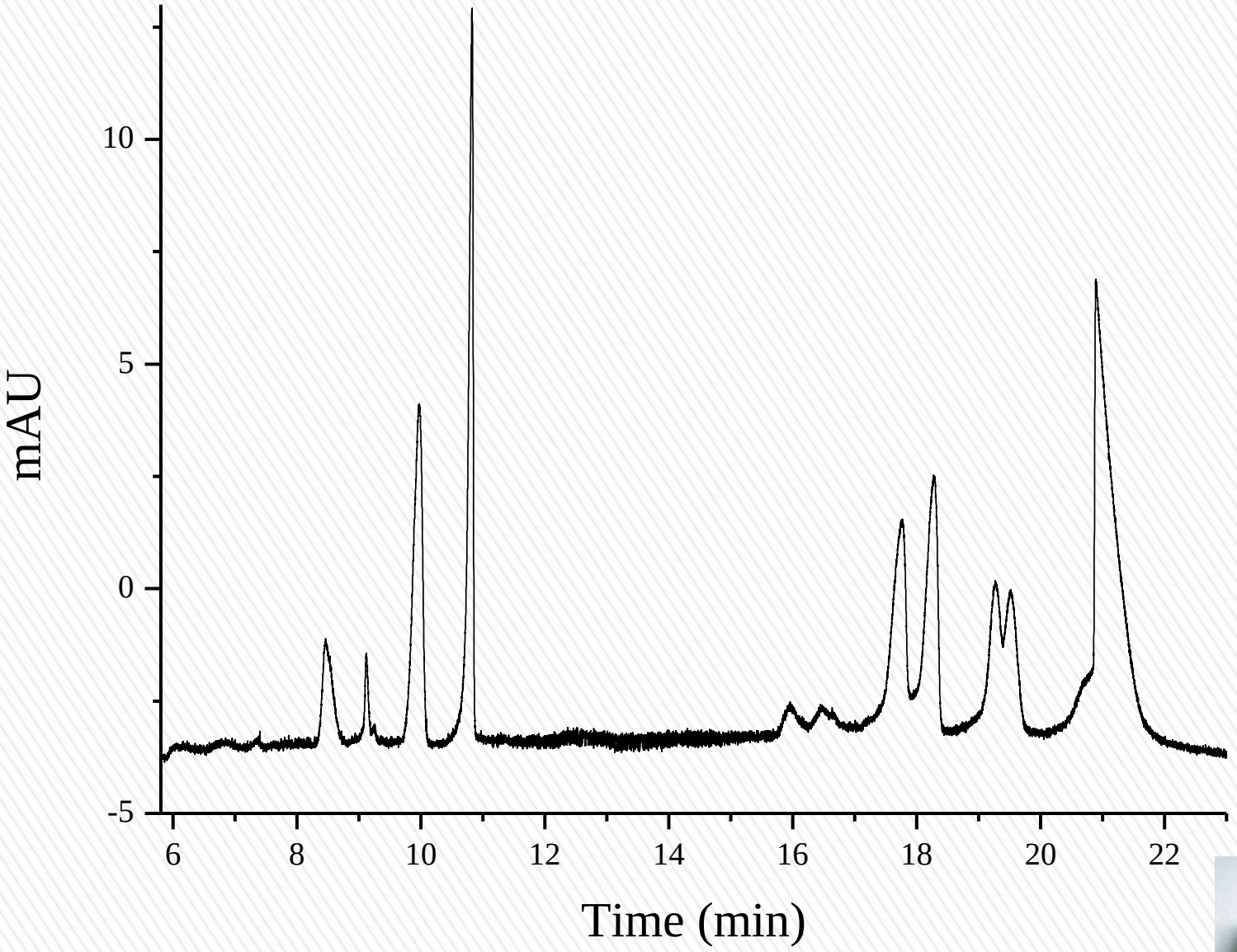
Micellar electrokinetic chromatography





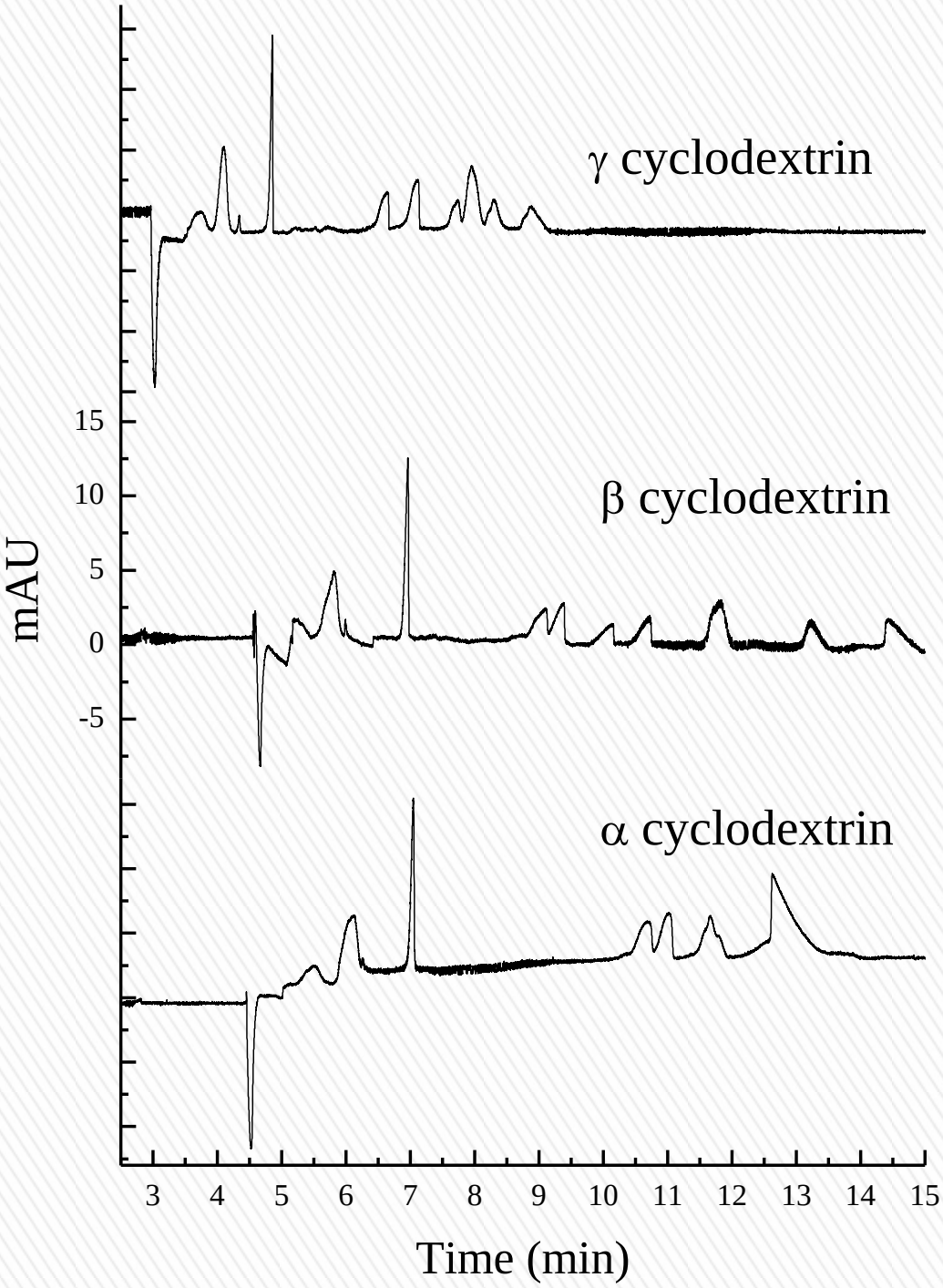
MEKC optimisation

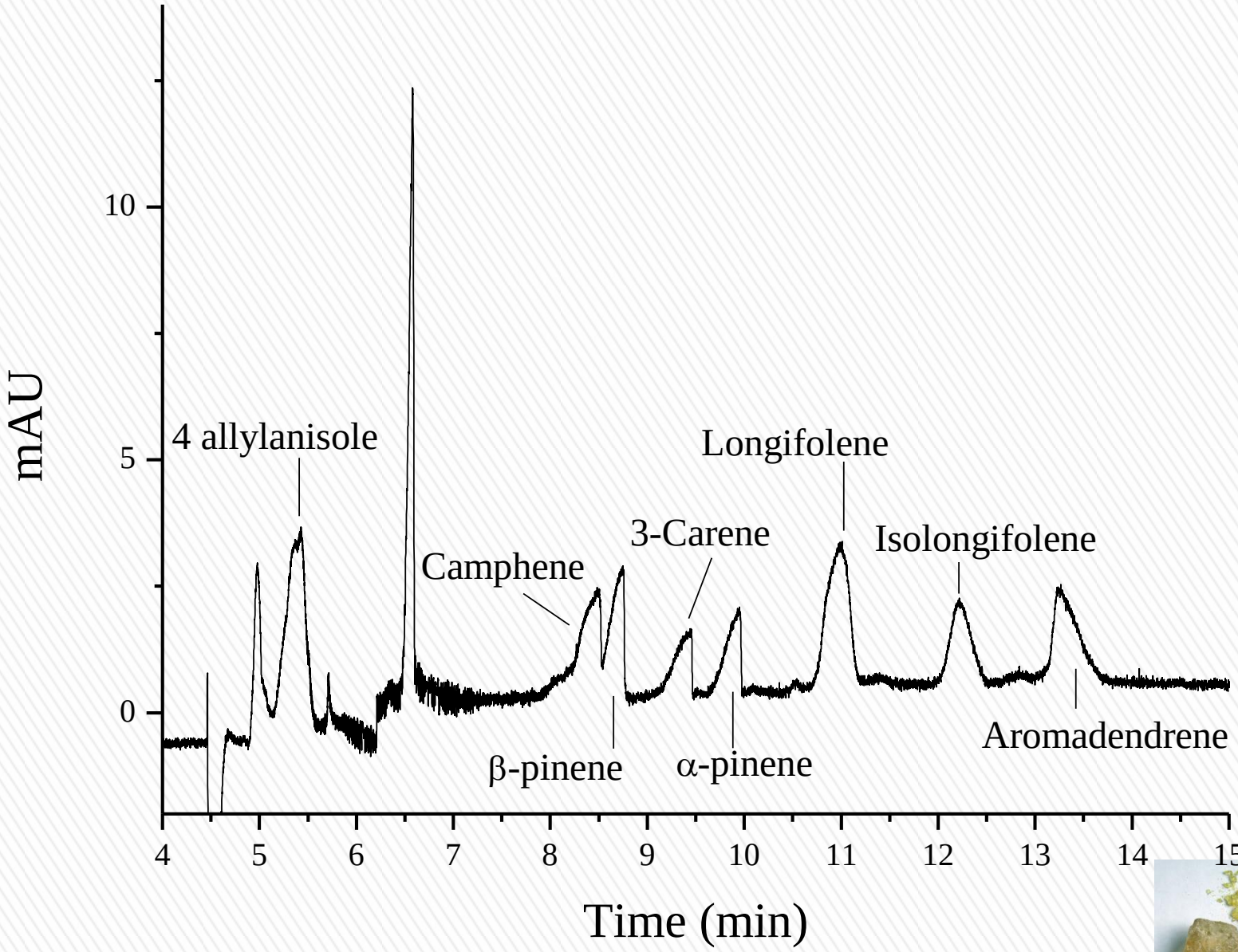
Buffer type	Tris	pH 8
Buffer conc	50 mM	
Surfactant conc	SDS	10 mM
Voltage	20 kV	



10 mM SDS 50 mM tris pH 8

CD-MEKC


γ cyclodextrin
β cyclodextrin
α cyclodextrin
mAU
15
10
5
0
-5
3
4
5
6
7
8
9
10
11
12
13
14
15
Time (min)



5 mM β-CD 10 mM SDS tris buffer

Summary

- Separation of resin acids using CE
- Application of method to rosin samples
  - Links between composition and rosin performance
- Separation of terpenes using CE
  - Application to rosin samples

Acknowledgements

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My lab colleagues

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