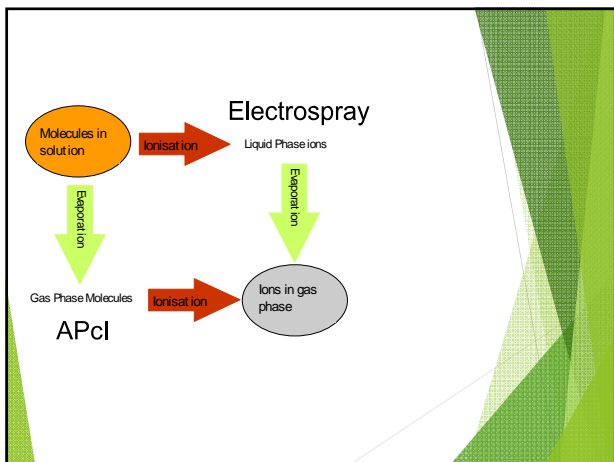


# LC/MS: massispektromeetri parameetrite optimeerimine

Anneli Kruve

## Ionisatsioonitüüp

- ▶ ESI
- ▶ APCI
- ▶ On olemas ka ESI ja APCI segu allikaid
- ▶ APPI
- ▶ Pole sageli komertsiaalselt olemas



**Table 1. Response Factors of Various Classes of Pesticides in Optimized Mobile Phases Using LC/MS in Full-Scan Mode\***

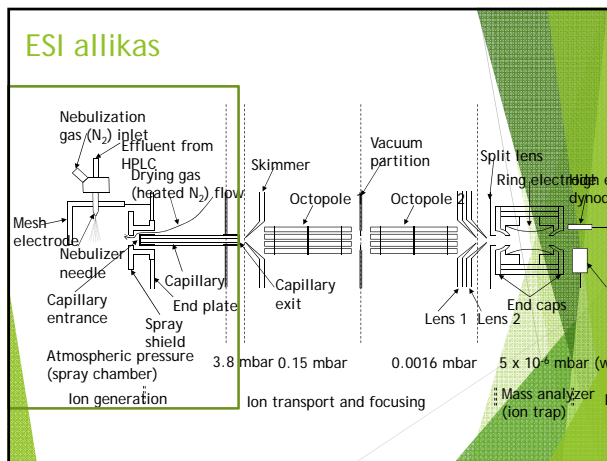
compound	APCI+	APCI-	ESI+	ESI-
phenylurea herbicides				
chlorambush	64	0	0	4
thiuron	57	10	7	5
fluometuron	64	7	6	6
isoproturon	100	0	14	0
linuron	14	7	7	3
thiourea herbicides				
atrazine	100	0	7	0
desmethylatrazine	50	0	3	0
dichloratrazine	25	0	7	0
cyprothiazole	71	0	7	0
tergafur	100	0	14	0
propazine	100	0	5	0
vinchlor	71	0	5	0
terbutylthio	100	0	5	0
triazolopyrimidone herbicides				
chlorfenvinphos	0	0	6	0
metolachlor	0	0	10	0
thiopyruvate	0	0	7	0
parquat	0	0	7	0
acetamide carbamates				
acetochlor EISA	0	0	0	11
acetochlor E5A	0	0	0	11
metolachlor E5A	0	0	0	14
acetochlor OXA	0	0	0	14
acetochlor OXA	0	0	0	14
acetochlor OXA	0	0	0	14
chlorophenoxycarbonyl herbicides				
dicamba	0	14	0	50
2,4-D	0	14	0	50
2,4-DEP	0	14	0	50
2,4,5-T	0	14	0	50
chlorophenols				
phenol	0	0	0	0
2-methylphenol	0	40	0	11
2,4-dimethylphenol	0	11	0	14
2,3,6-trimethylphenol	0	14	0	14
4-chloro-2-methylphenol	0	14	0	5
2,4,5-trimethylphenol	0	50	0	7
alkyl sulfate surfactant				
sodium dodecyl sulfate	0	0	0	30

Chemical structures are shown for various compounds: chlorambush, thiuron, fluometuron, isoproturon, linuron, atrazine, desmethylatrazine, dichloratrazine, cyprothiazole, tergafur, propazine, vinchlor, terbutylthio, chlorfenvinphos, metolachlor, thiopyruvate, parquat, acetochlor EISA, acetochlor E5A, metolachlor E5A, acetochlor OXA, acetochlor OXA, dicamba, 2,4-D, 2,4-DEP, 2,4,5-T, phenol, 2-methylphenol, 2,4-dimethylphenol, 2,3,6-trimethylphenol, 4-chloro-2-methylphenol, 2,4,5-trimethylphenol, and sodium dodecyl sulfate.

Thurman 2001 *Anal. Chem.* 73, 5441-5449

## ESI vs APCI

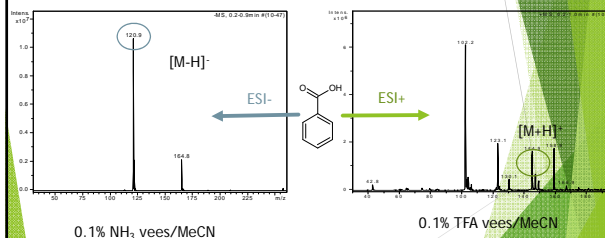
<p><b>ESI</b></p> <ul style="list-style-type: none"> <li>▶ pKa</li> <li>▶ Elektronegatiivsus</li> <li>▶ Hüdrofoobsus</li> </ul>	<p><b>APCI</b></p> <ul style="list-style-type: none"> <li>▶ Lenduvus</li> <li>▶ Prootonafiivsus</li> <li>▶ gaasifaasis/happelisus</li> <li>▶ gaasifaasi</li> </ul>
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### Ioonaalika parameetrid

- ▶ Polaarsus ESI+ või ESI-
- ▶ Pihustusgaas
- ▶ Kuivatusgaas
- ▶ Kapillaaripinge

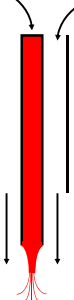
### ESI+ või ESI-



### ESI PIHUSTI

Analüüsiv vedelik

Pihustusgaas



- 1) Fikseeritud kaugusega (robustsem)
  - 2) Muudetava kaugusega (võimalik tundlikkust reguleerida)
- Optimaalne kaugus sõltub vedeliku voolukiirusest

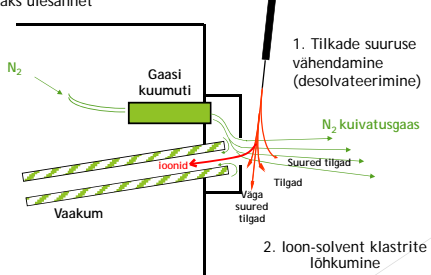
### Vaikeparameetrid

Electrospray Ionization<sup>1</sup>

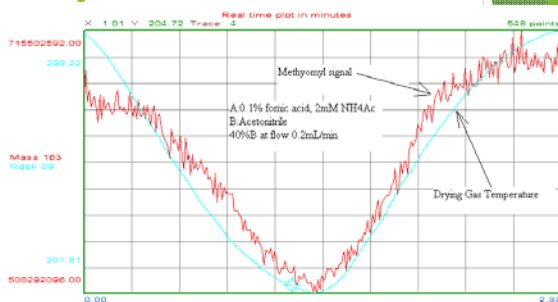
HPLC Flow Rate (ul/min)	Nebulizer Spacer <sup>2</sup>	Nebulizer Pressure (psi)	Drying Gas Flow (l/min)	Drying Gas Temp (°C)	Capillary Voltage (V)
1 – 10	Not Installed	10 – 15	4	325	3500 <sup>3</sup>
10 – 50	Not Installed	15 – 20	5	325	
50 – 200	Installed <sup>3</sup>	20 – 40	8	350	
200 – 500	Installed	30 – 50	8 – 10	350	
500 – 1000	Installed	50 – 70	10 – 12	350	

### KUIVATUSGAAS

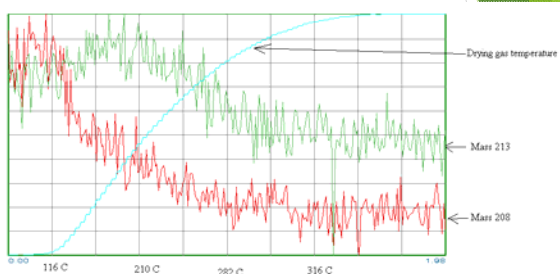
Kuivatusgaasil on kaks ülesannet



### Kuivatusgaasi temperatuuri mõju

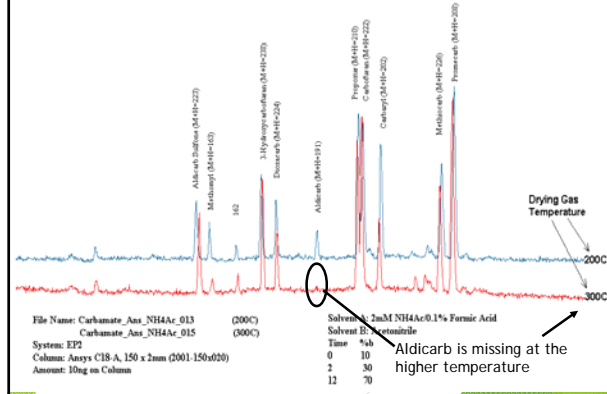


## Kuivatusgaasi temperatuuri mõju



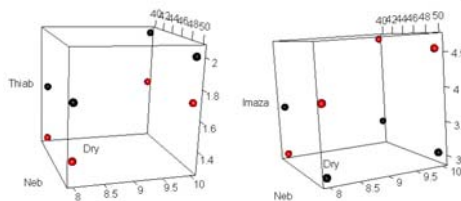
## LC/MS Analysis of Carbamates Mixture

(Comparison of Drying Gas Temperature)



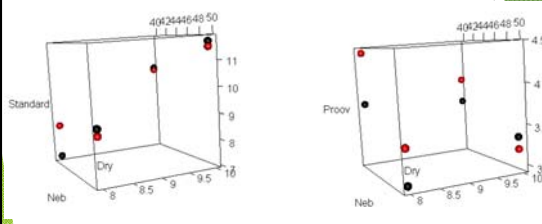
## Kasulik on uurida mitut parameetrit koos

1. Seose erinevate parameetrite vahel ei ole alati lineaarne
2. Kõik ained ei käitu samamoodi!



Mustad täpid - kapillaari pinge 150V, Punased täpid - kapillaaripinge 250V

## Kas optimeerida solvendis või reaalsetes proovides?

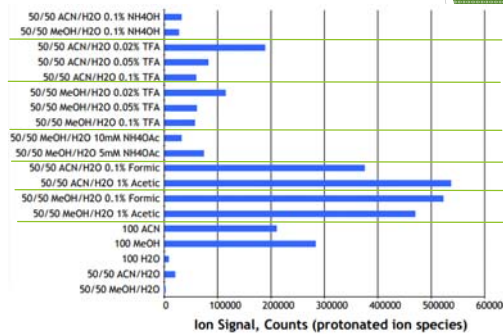


Mustad täpid - kapillaari pinge 150V, Punased täpid - kapillaaripinge 250V

## Lisandid

- ▶ pH reguleerimine
  - ▶ Lenduv puhver
  - ▶ Vastavalt analüüdi pKa-le
- ▶ Pindpinevuse vähendamine
- ▶ Võib olla vajalik LC meetodit uuesti optimeerida
  - ▶ Parem järjekord - optimeerida ionisatsioon enne ja kromatograafia!

## andid



## Lisandid

