



# Iontová chromatografie v tradičních i nových směrech

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# Thermo Scientific - nabídka IC systémů

RFIC

HPIC



Dionex Easion



Dionex Aquion



Dionex Integrion



Dionex ICS-6000

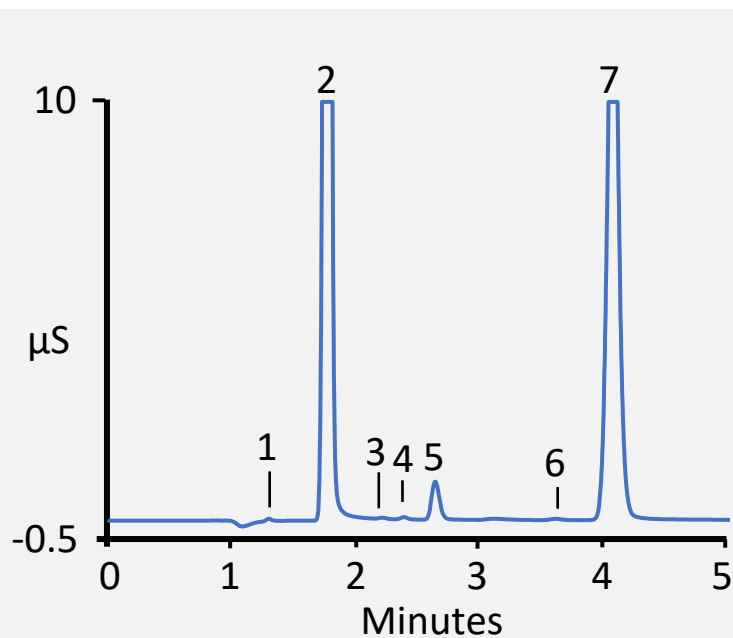


**Téma přednášky :**  
**Aplikace tradiční**  
**bromičnany, chloritany, chlorečnany**  
**HAA**  
**pesticidy**  
**PFAS**  
**Příprava a zpracování vzorku**



# Klasické anionty – eluent uhličitán/hydrogenuhličitán

## Municipal Drinking Water



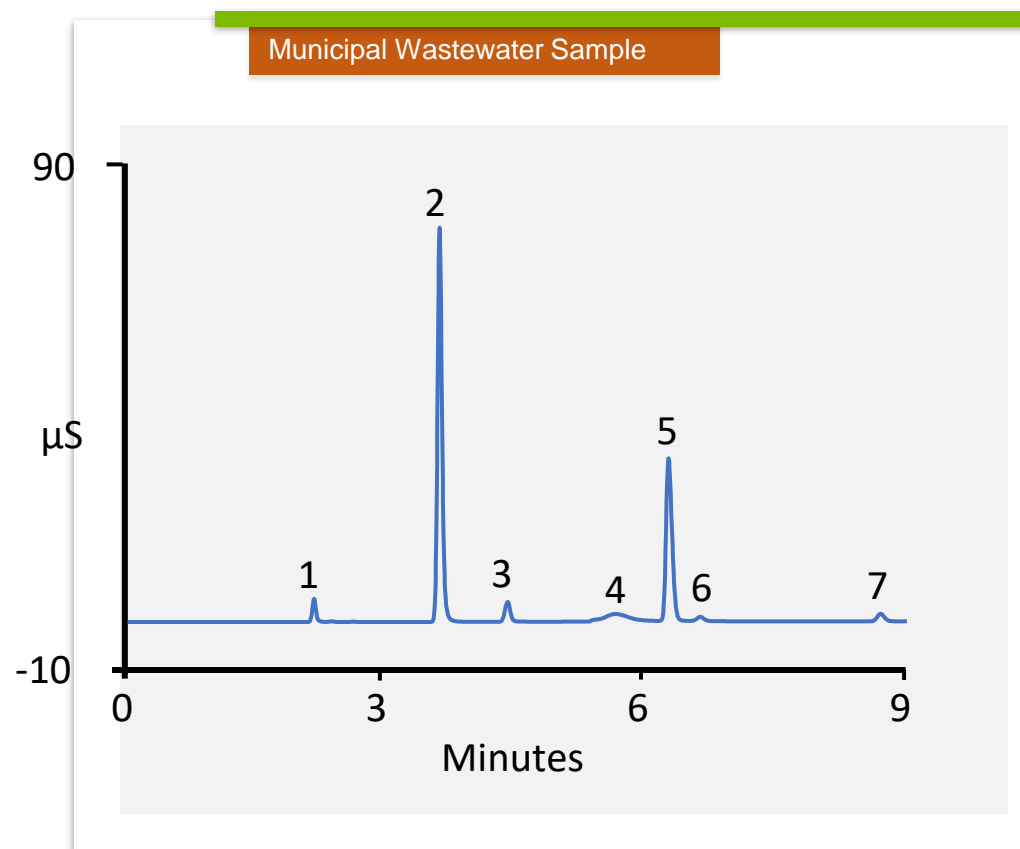
## Conditions

Columns: Dionex IonPac AG22-Fast-4 $\mu\text{m}$   
Dionex IonPac AS22-Fast-4 $\mu\text{m}$ ,  
2  $\times$  150 mm  
Eluent: 4.5 mM Sodium Carbonate  
1.4 mM Sodium Bicarbonate  
Flow Rate: 0.5 mL/min  
Inj. Volume: 2.5  $\mu\text{L}$   
Column Temp.: 30  $^{\circ}\text{C}$   
Detection: Suppressed conductivity,  
Dionex AERS 500 Carbonate, 2 mm  
17 mA, recycle mode

## Peaks:

1. Fluoride	< 1	5. Nitrate	1.0	mg/L
2. Chloride	120	6. Phosphate	< 2	
3. Nitrite	< 1	7. Sulfate	56	
4. Bromide	< 1			

# Klasické anionty – eluent hydroxid



## Conditions

Columns: Dionex IonPac AG18-Fast-4µm  
Dionex IonPac AS18-Fast-4µm,  
4 × 150 mm  
KOH Gradient: 15–44 mM (0.2 to 6 min)  
Eluent Source: Dionex EGC 500 cartridge with Dionex  
CR-ATC 600 trap and Dionex high  
pressure degasser devices

Flow Rate: 1 mL/min

Inj. Volume: 10 µL

Column Temp.: 30 °C

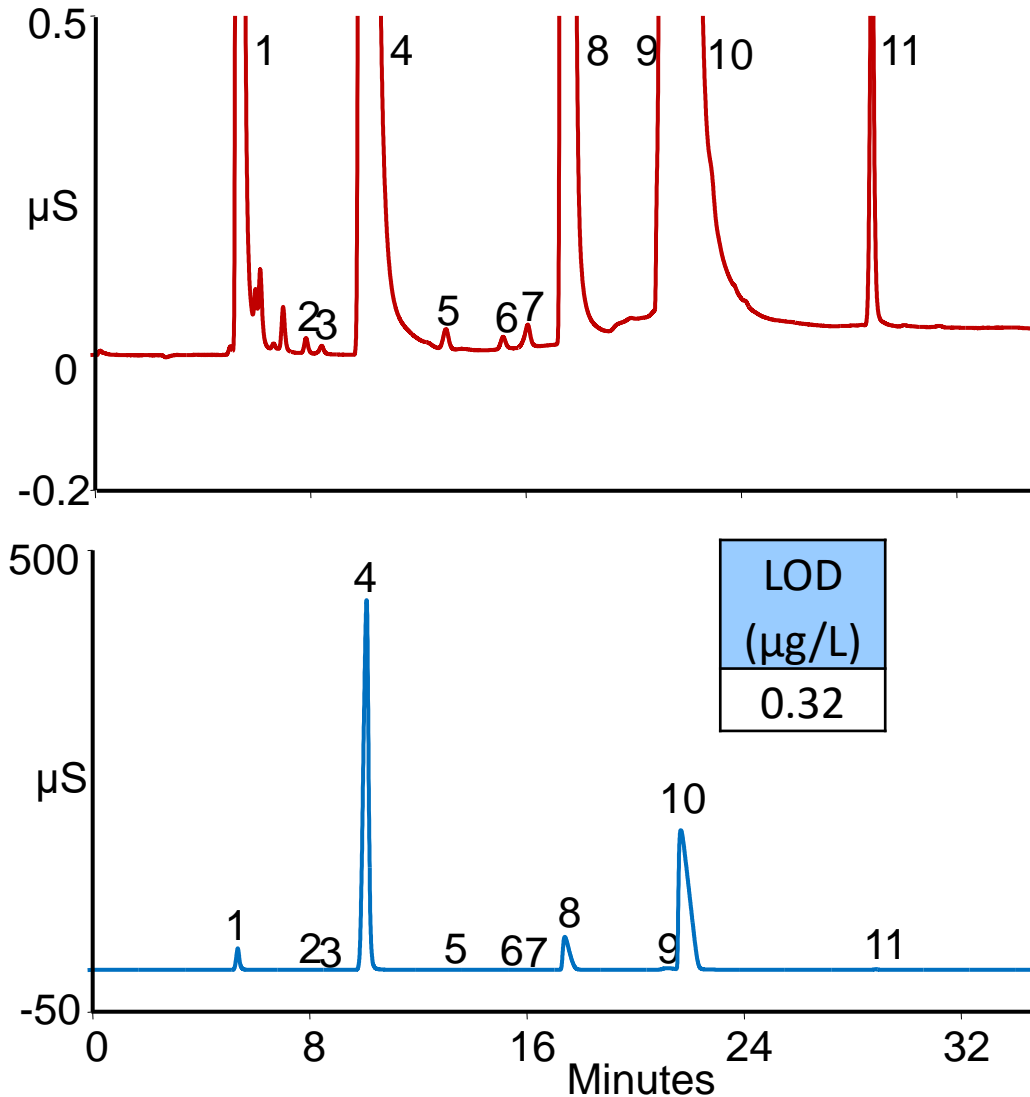
Detection: Suppressed conductivity, Dionex  
AERS 500, 4 mm, 109 mA, recycle

Sample Prep.: 5x dilution with deionized water

### Peaks:

1. Fluoride	1.0	5. Sulfate	51.8	mg/L
2. Chloride	90.6	6. Nitrate	2.6	
3. Nitrite	1.0	7. Phosphate	0.36	
4. Carbonate	--			

# Stanovení stopových množství bromičnanu na CD

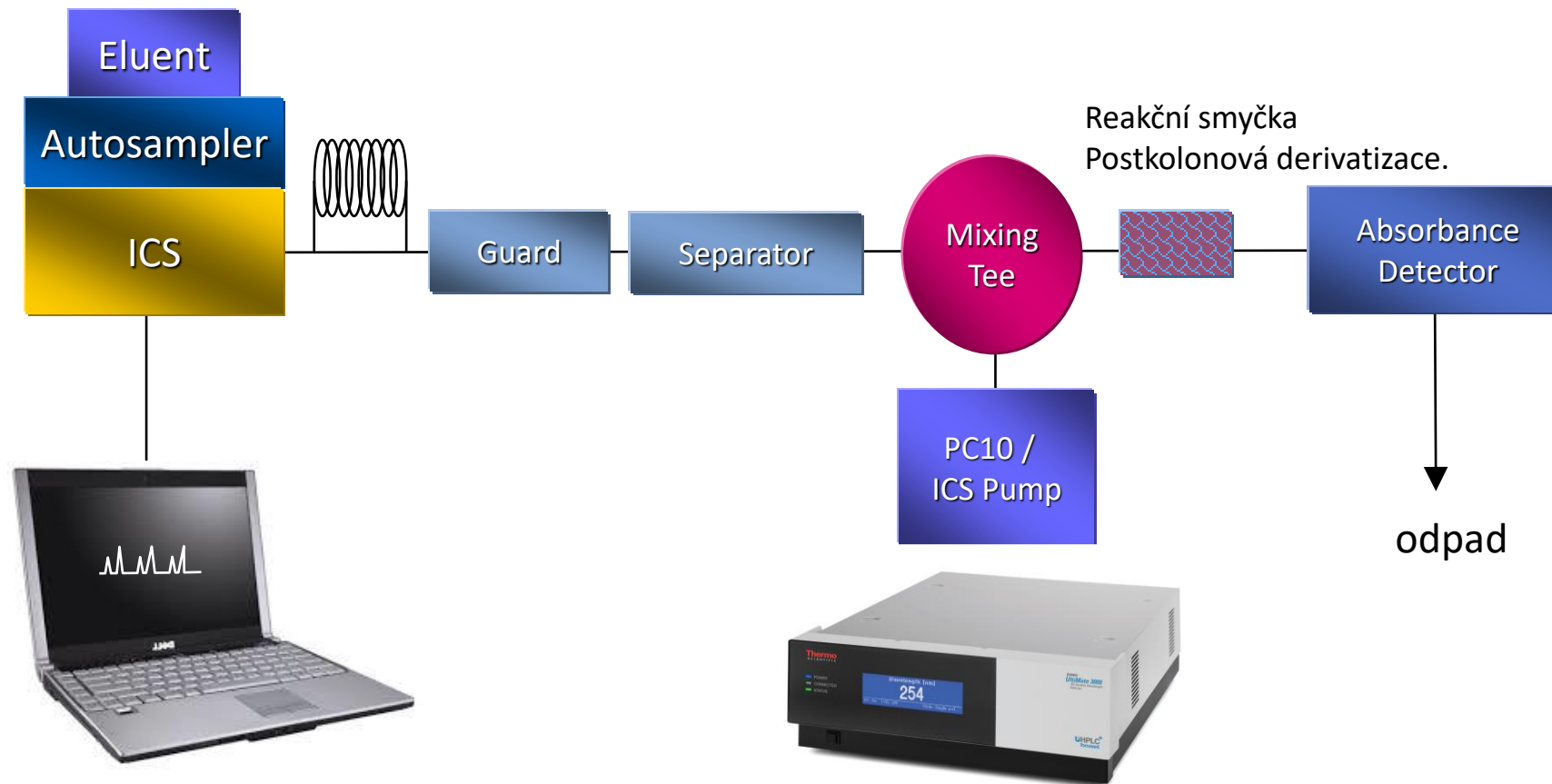


System: Thermo Scientific™ Dionex™ ICS-5000+ HPIC system  
 Column: Thermo Scientific™ Dionex™ IonPac™ AS19-4µm + guard (4 × 250 mm)  
 Eluent: 10 mM KOH from 0 to 10 min, 10–45 mM KOH from 10 to 25 min  
 Eluent Source: Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge  
 Flow Rate: 1.0 mL/min  
 Inj. Volume: 200 µL  
 Temperature: 30 °C  
 Detection: Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500 suppressor, 4 mm AutoSuppression, recycle mode  
 Sample: Simulated Drinking Water

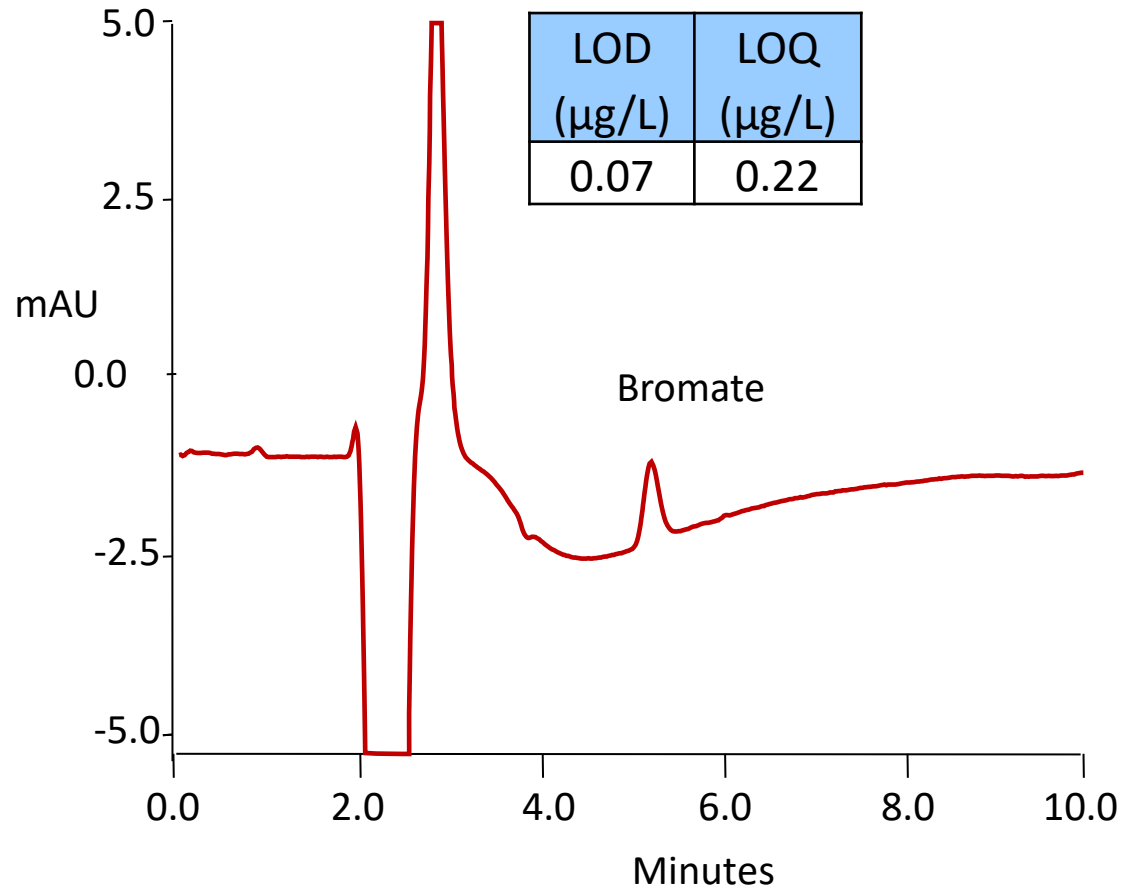
Peaks:	Concentration (mg/L)
1. Fluoride	1.0
2. Chlorite	0.005
3. Bromate	0.005
4. Chloride	50.0
5. Nitrite	0.005
6. Chlorate	0.005
7. Bromide	0.005
8. Nitrate	10.0
9. Carbonate	25.0
10. Sulfate	50.0
11. Phosphate	0.20

**Doporučení - hydroxid**

# Druhá varianta – bromičnany - UV detektor



# Bromičnany pomocí okyseleného eluentu na UV



Column: Thermo Scientific™ Dionex™  
CarboPac™ PA1  
(4 × 250 mm)

Eluent: 200 mmol/L MSA

Flow: 1 mL/min

Injection vol.: 500  $\mu\text{L}$

Detection: UV 352 nm (after PCR)

Temperature: 30 °C

PCR:

Solution A: 0.27 mol/L KI, 0.05 mmol/L  
(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O

Flow: 0.3 mL/min

Reaction coil: 375  $\mu\text{L}$

Bromate: 1.2  $\mu\text{g/L}$

Není interference s chromitanem



# Halooctové kyseliny (HAA5, HAA6Br, a HAA9)

	Acid	HAA	Formula	pK <sub>a</sub>
HAA5	Monochloroacetic acid	MCAA	ClCH <sub>2</sub> CO <sub>2</sub> H	2.86
	Dichloroacetic acid	DCAA	Cl <sub>2</sub> CHCO <sub>2</sub> H	1.25
	Trichloroacetic acid	TCAA	Cl <sub>3</sub> CCO <sub>2</sub> H	0.63
HAA9 HAA6Br	Monobromoacetic acid	MBAA	BrCH <sub>2</sub> CO <sub>2</sub> H	2.87
	Dibromoacetic acid	DBAA	Br <sub>2</sub> CHCO <sub>2</sub> H	1.47
	Tribromoacetic acid	TBAA	Br <sub>3</sub> CCO <sub>2</sub> H	0.66
	Bromochloroacetic acid	BCAA	BrClCHCO <sub>2</sub> H	1.39
	Chlorodibromoacetic acid	CDBAA	Br <sub>2</sub> ClCCO <sub>2</sub> H	1.09
	Bromodichloroacetic acid	BDCAA	Cl <sub>2</sub> BrCCO <sub>2</sub> H	1.09

UCMR\* 4 (2017–2021, 30 contaminants)

Regulated (EPA)

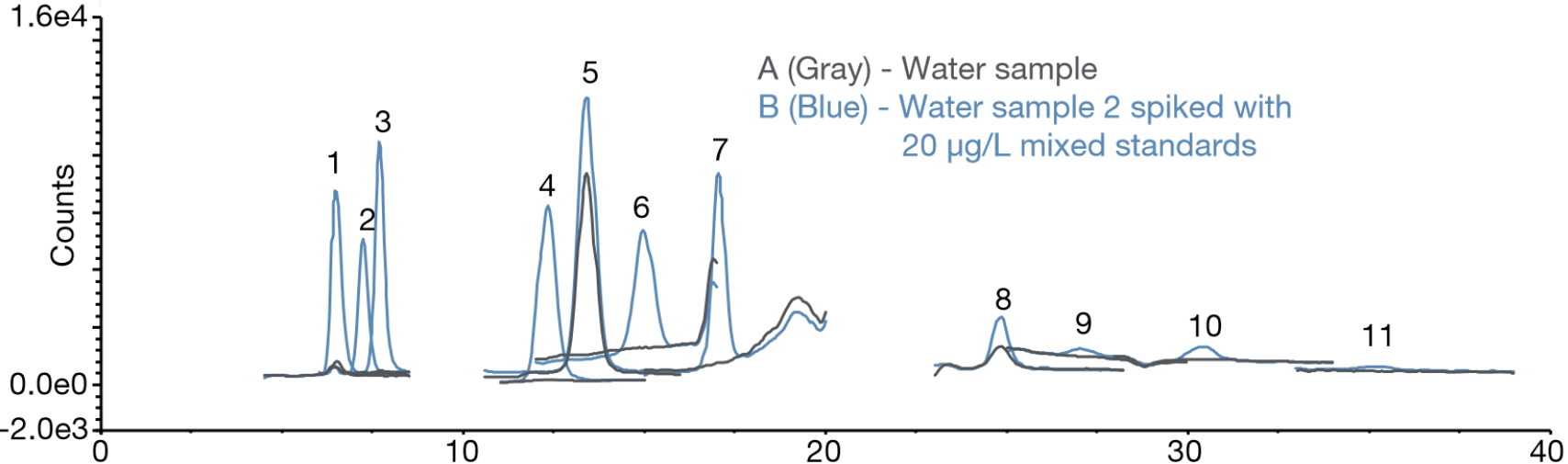
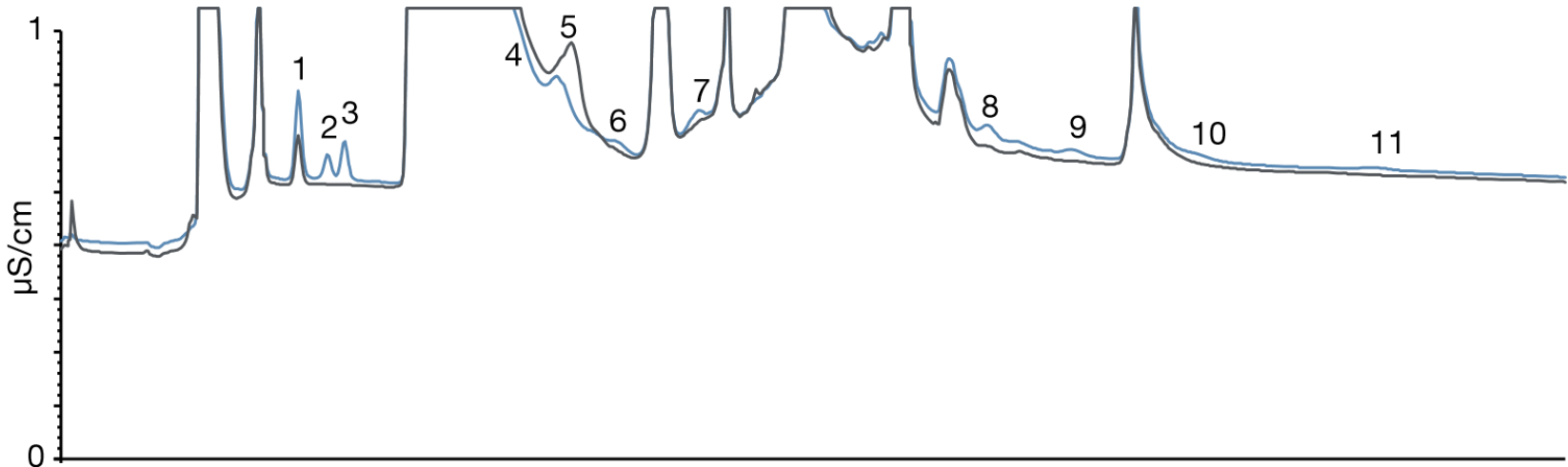
*\*Unregulated Contaminant Monitoring Rule*

# Proč IC?

## Proč ICMS ?

- výhody
  - Přímý nástřik metod s matričním efektem
  - Eliminace kapalina – kapalina extrakce,
  - Eliminace nutnosti derivatizace
  - Eliminace co-eluce - MS je selektivní detektor
  - MS/MS poskytuje konfirmační informaci
  - Plná automatizace
  - výtěžnost > 90%
- limitace
  - Náklady na nákup MS
  - Analyty jsou teplotně labilní

# Voda s a bez naspikování 20 µg/L 9 HAA, bromičnanem a dalaponem



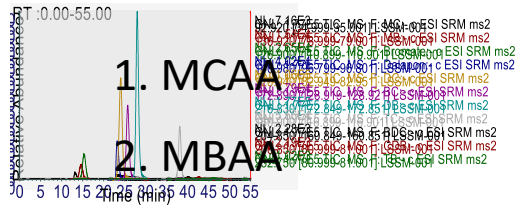
A (Gray) - Water sample  
 B (Blue) - Water sample 2 spiked with 20 µg/L mixed standards

No.	Peak	RT (min)	Conc. (µg/L)	
			A	B
1	MCAA	6.5	1.5	22.9
2	MBAA	7.2	ND	21.8
3	Bromate	7.7	ND	23.2
4	Dalapon	12.3	ND	20.4
5	DCAA	13.4	22.3	43.4
6	BCAA	15.0	ND	20.8
7	DBAA	17.1	ND	20.7
8	TCAA	24.8	16.4	37.8
9	BDCAA	27.0	ND	18.6
10	CDBAA	30.4	ND	21.0
11	TBAA	35.1	ND	13.1

A (Gray): Water sample 2  
 B (Blue): Water sample 2 spiked with 20 µg/L mixed standards  
 ND: Not detectable



# Přeložené chromatogramy



3. Bromate

4. Dalapon

5. DCAA

6. BCAA

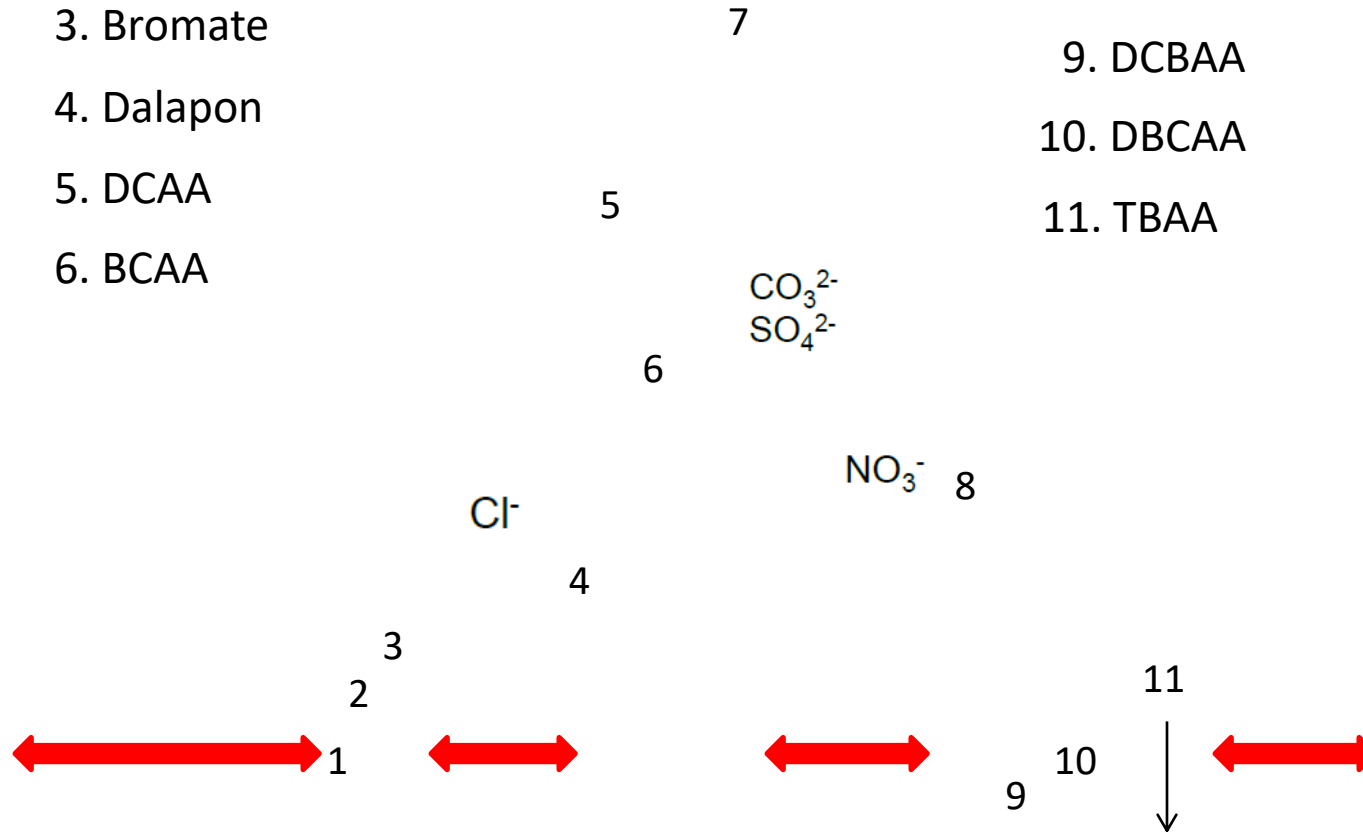
7. DBAA

8. TCAA

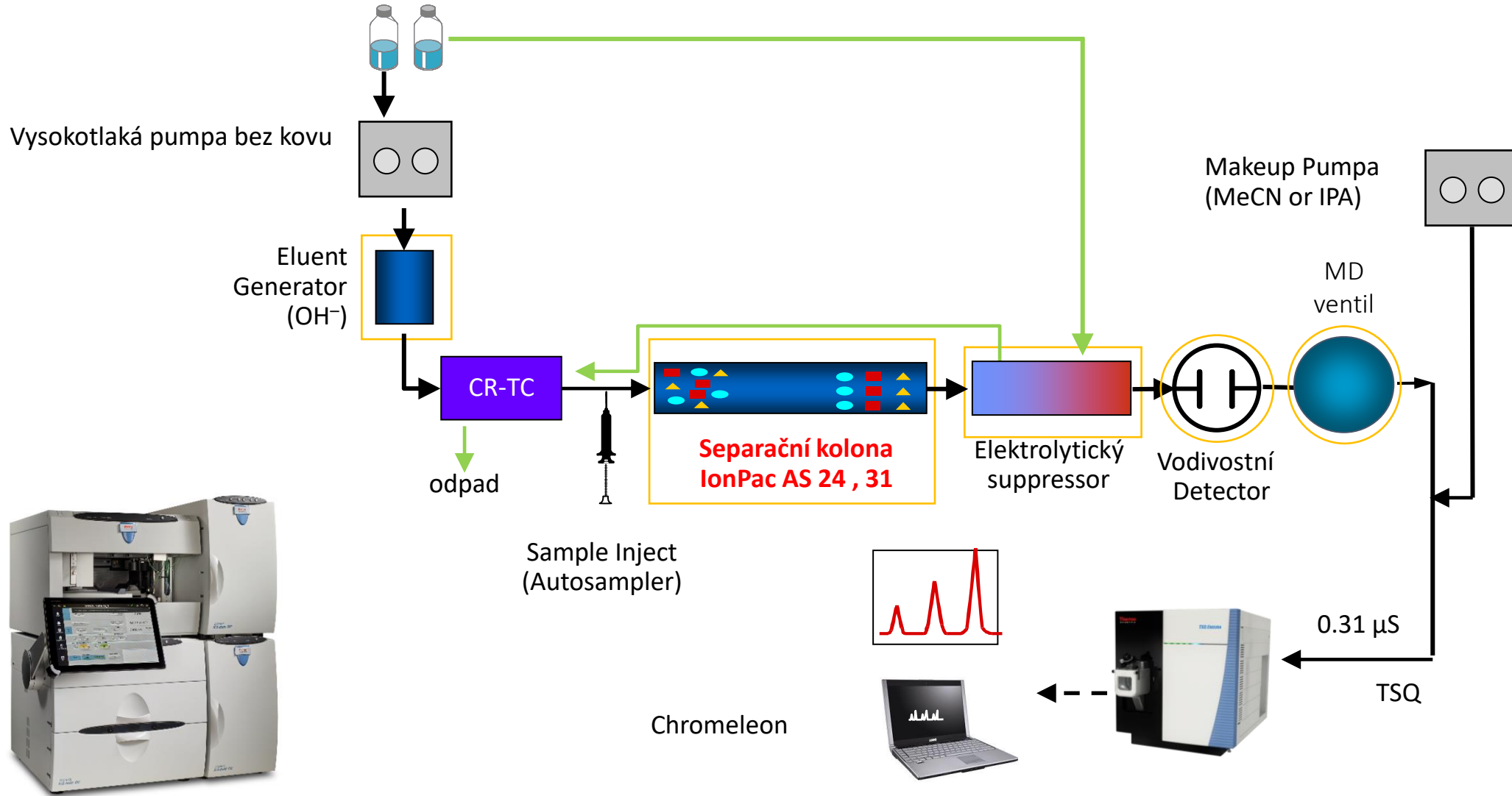
9. DCBAA

10. DBCAA

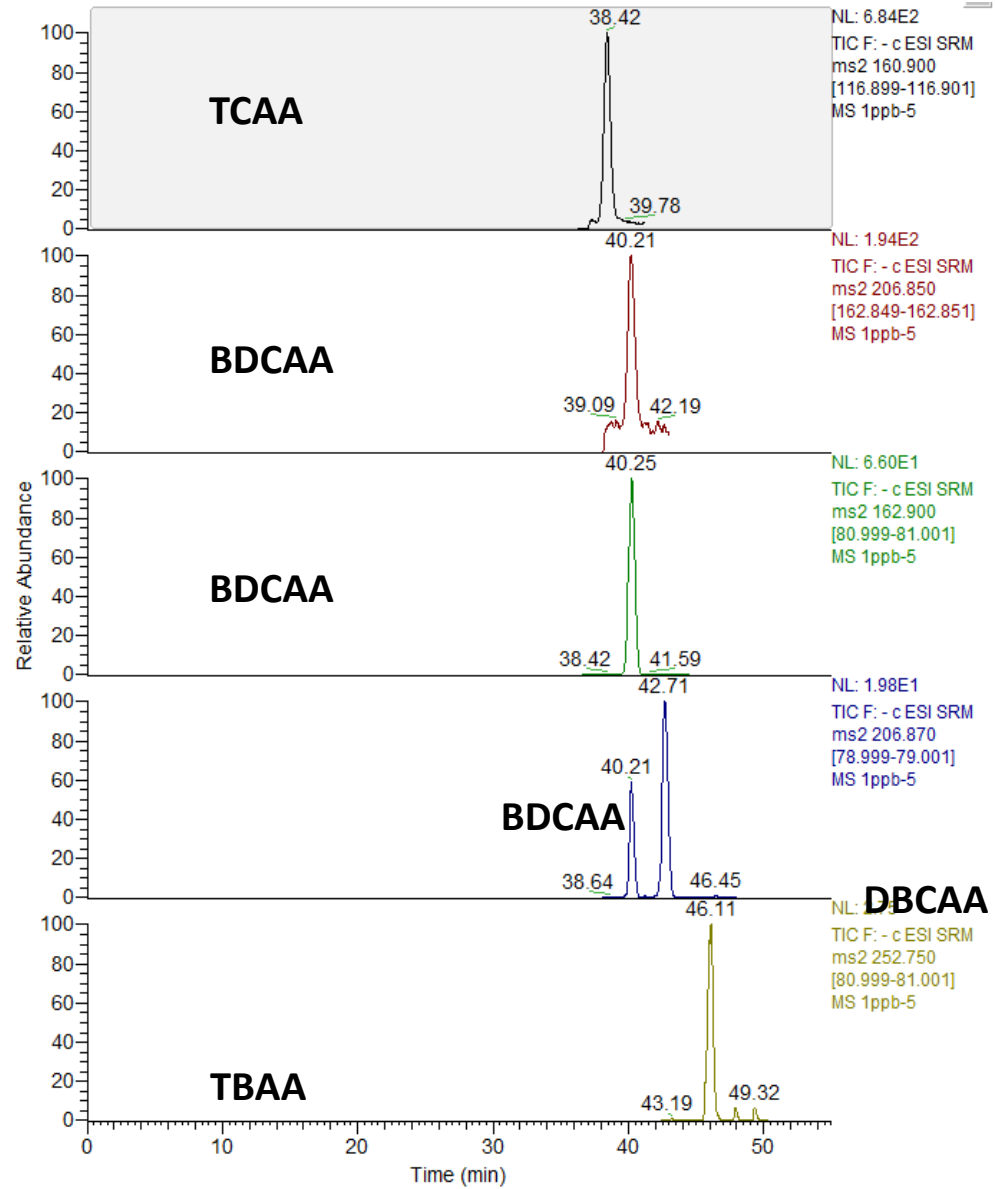
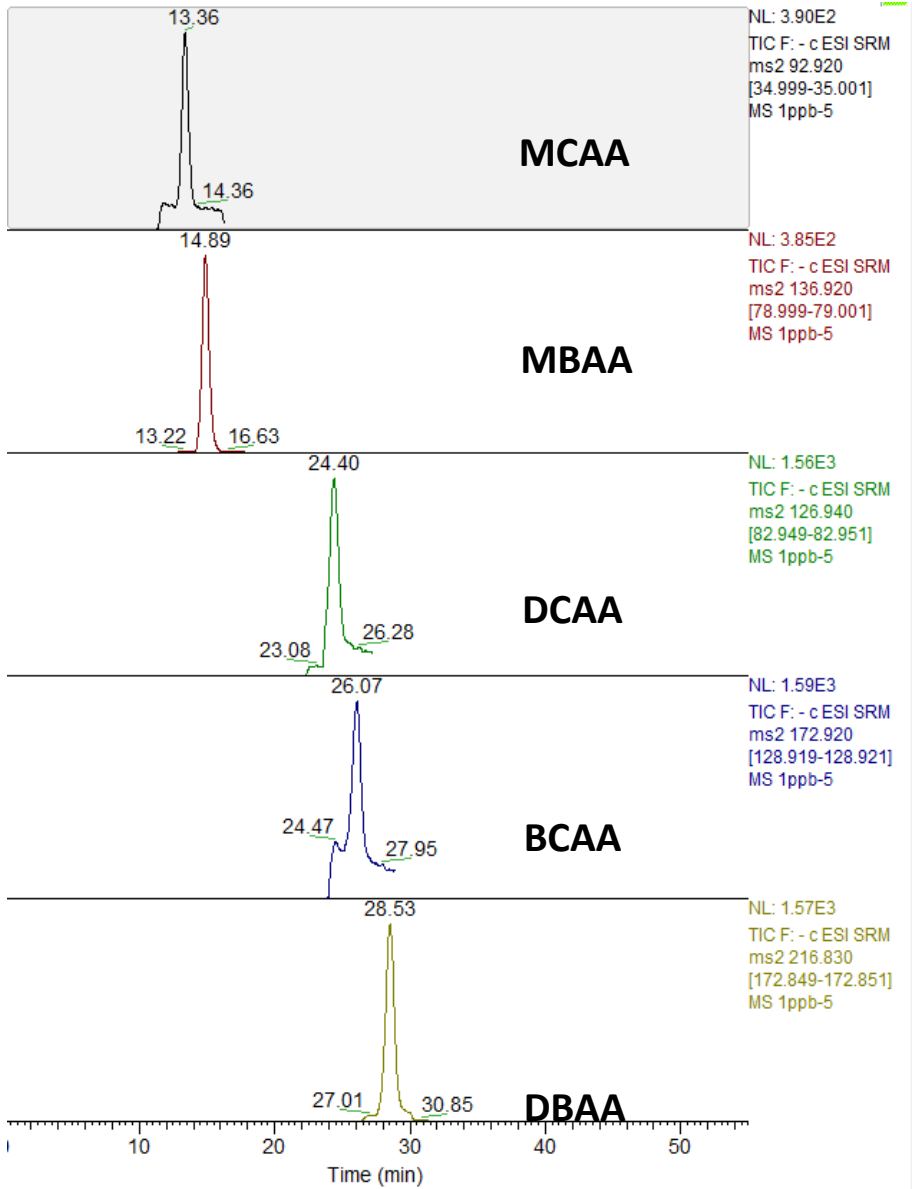
11. TBAA



# IC-MS (/MS) HAA schéma



# 1 µg/l HAA Standard



# Detekční limit pro HAA, bromičnan a dalapon při použití IC

IC – ESI MS/MS

MDL (µg/L, n=7)	Abbreviation	EPA Calculated DL	GC-ECD	AS24 Calculated DL	AS31 Calculated DL	IC XIC 2D IC	IC-MS
Monochloroacetic acid	MCAA	0.2	0.273	0.105	0.19	0.085	0.1
Monobromoacetic acid	MBAA	0.064	0.204	0.104	0.021	0.1	0.03
Bromate	Bromate	0.02	N.D	0.059	0.014		0.12
Dalapon	Dalapon	0.038	N.D	0.05	0.079		0.12
Dichloroacetic acid	DCAA	0.055	0.242	0.044	0.019	0.41	0.033
Bromochloroacetic acid	BCAA	0.11	0.251	0.059	0.086	0.3	0.16
Dibromoacetic acid	DBAA	0.015	0.066	0.021	0.009	0.09	0.16
Trichloroacetic acid (163/119)	TCAA	0.09	0.079	0.033	0.073	0.26	0.67
Bromodichloroacetic acid	BDCAA	0.05	0.091	0.141	0.087	0.29	2.79
Chlorodibromoacetic acid	DBCBA	0.041	0.468	0.214	0.19	0.055	1.04
Tribromoacetic acid	TBAA	0.067	0.82	0.159	0.067	0.28	4.55

# Polární pesticidy pomocí IC MS (MSMS)

- Stanovení bez derivatizace

Fosetyl-Al

Clopyralid

AMPA

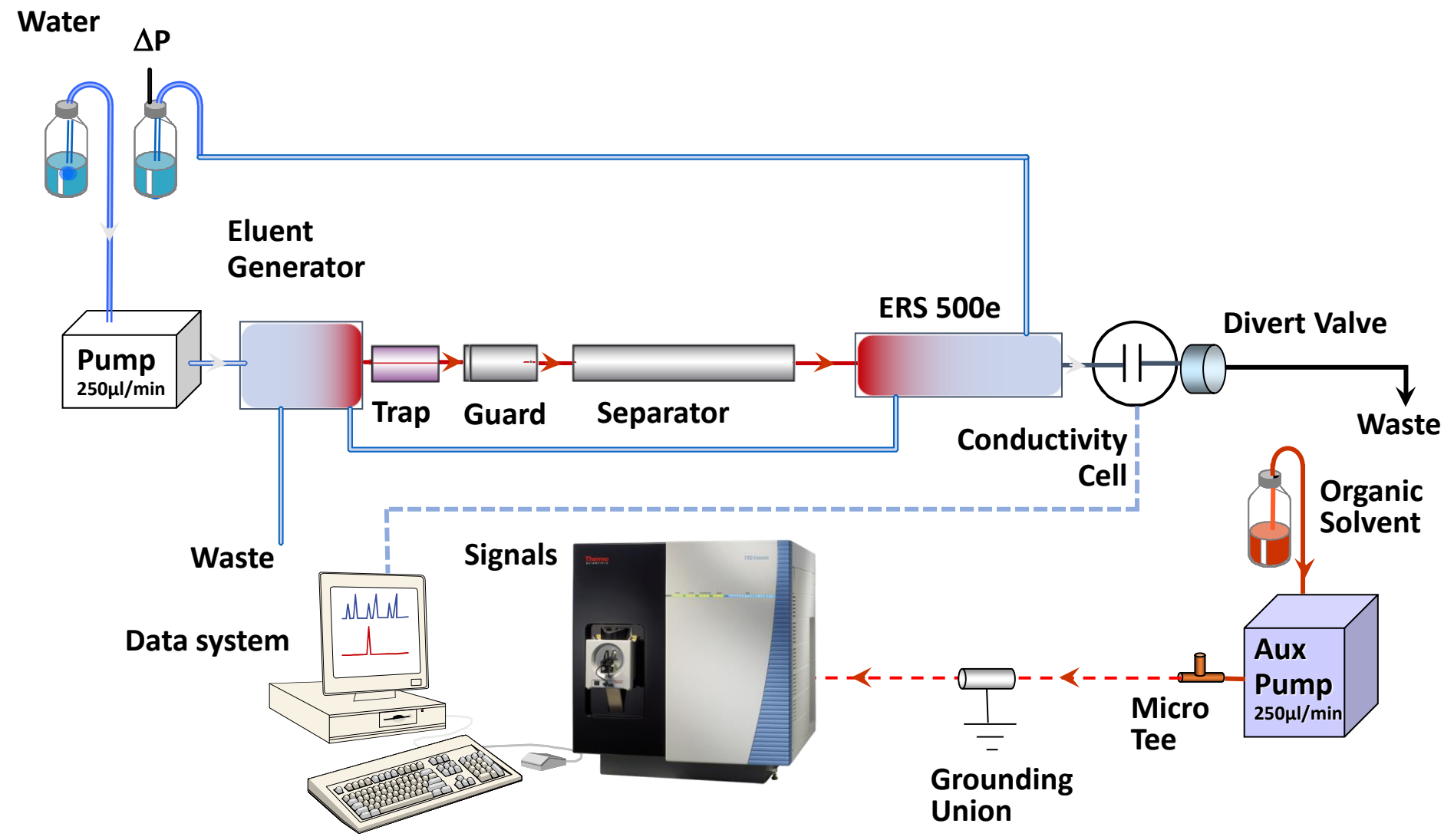
Glyfosat

Glufosinat

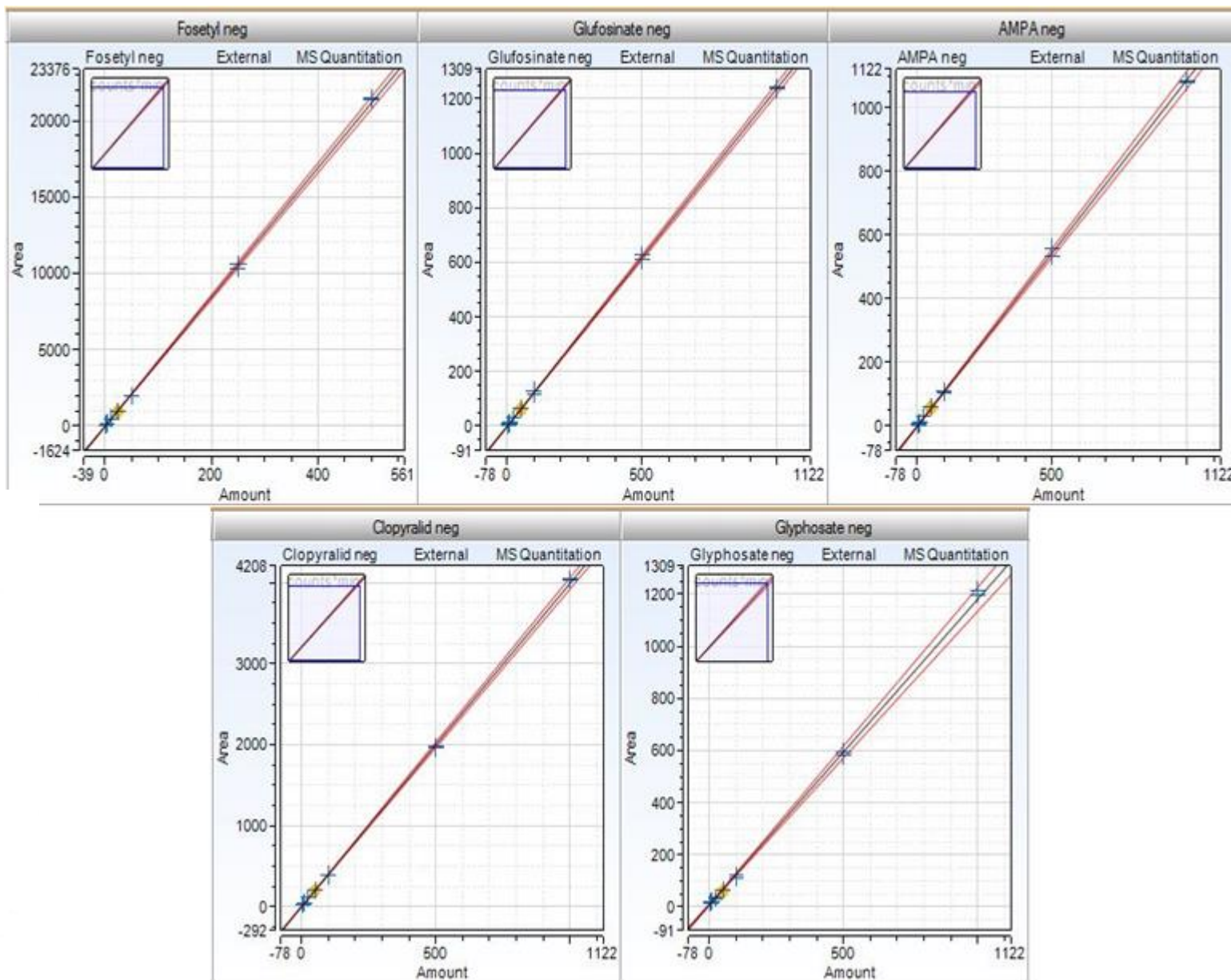




# IC MS (MS/MS)



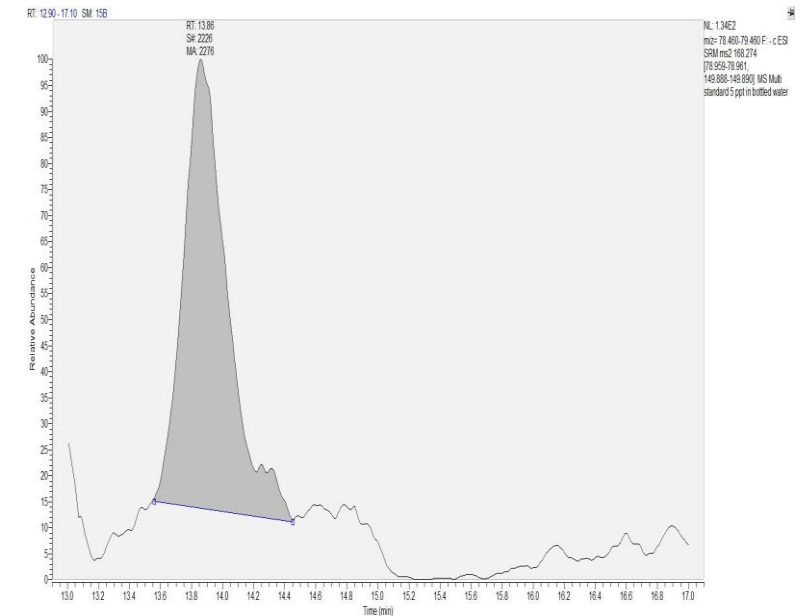
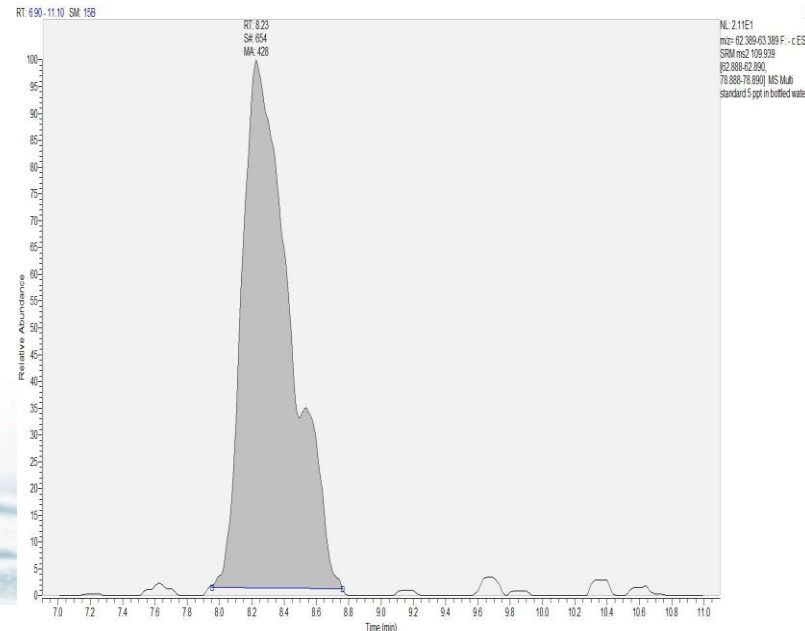
# Kalibrační křivky v pitné vodě



# Evian voda LOD a LOQ

Name	LOD [ppt]	LOQ [ppt]	RSD % (10 ppt) level
Fosetyl-Al	1	2.5	5
Clopyralid	10	50	9
AMPA	2	5	9
Glyphosate	5	10	15
Glufosinate	2	5	4

**AMPA a GLYFOSAT**  
**5 ppt**



# Spojení HPLC a IC s QQQ



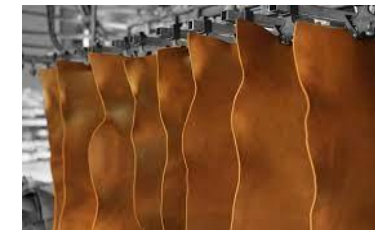
# PFAS - Per- a PolyFluorinated Alkyl Substances

Kombinace spalovací techniky s iontovým chromatografem

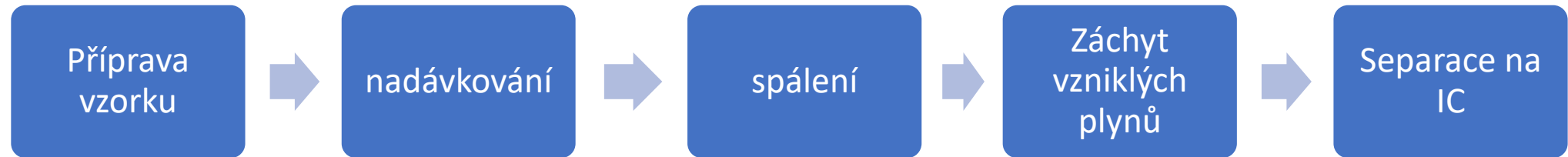


# Zdroje PFAS

- Hlavní výrobní a průmyslové zdroje
- Stavebnictví a stavební materiály
- Kabel a elektroinstalace
- Povrchová úprava a pokovování kovů
- Výroba průmyslových povrchově aktivních látek a fluoropolymerů
- Papírové výrobky a obaly
- Fotolitografie/průmysl polovodičů
- Textil, kůže a oděvy
- Koberec a nábytek
- Hasicí pěny třídy B obsahující fluor
- Zařízení pro nakládání s pevným odpadem
- Zbytky z čištění odpadních vod



# Princip stanovení



vzorek	spálení	detekce	Detekce na IC
<b>Halogens</b>	<b>H-X, X<sub>2</sub></b>	<b>F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup></b>	<p>The chromatogram displays detector response in <math>\mu\text{S/cm}</math> over a 19-minute period. The y-axis ranges from 0.5 to 5.5. The x-axis is labeled in minutes (min). Several peaks are identified with their retention times: Fluoride at 3.96 and 4.65 minutes, Chloride at 5.18 minutes, Bromide at 7.70 and 8.81 minutes, and Sulfate at 14.16 minutes.</p>

# Přístroje pro přípravu vzorku

Pevný vzorek



ASE™ 350  
Accelerated Solvent Extractor



EXTREVA™ ASE™  
Accelerated Solvent  
Extractor

Kapalina



AutoTrace™ 280  
Solid-Phase Extraction  
(SPE) Instrument



# EXTREVA ASE system



## Zjednodušená extrakce vzorku

Kombinuje **extrakci vzorku, čištění a zakonzentrování**



## 2 in 1

Extrakce a zakonzentrování v 1 systému



## Zvýšená produktivita laboratoře

Paralelní extrakce až 4 vzorků najednou  
snižuje náklady na vzorek



## Kompletní pracovní postup od vzorku po lahvičku

True **walk-away** technology

# Water and Environmental Analysis Online User Meeting,



Emerging contaminants  
and evolving regulations:  
Meeting environmental  
testing demands

Online User Meeting  
June 27-28

 Register now

Presentation topics include:

- PFAS
- Microplastics
- Disinfection by-products
- Haloacetic acids
- Trace metals
- Screening unknown contaminants
- Biotoxins
- Advances in LC and GC automation

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Děkuji za pozornost