

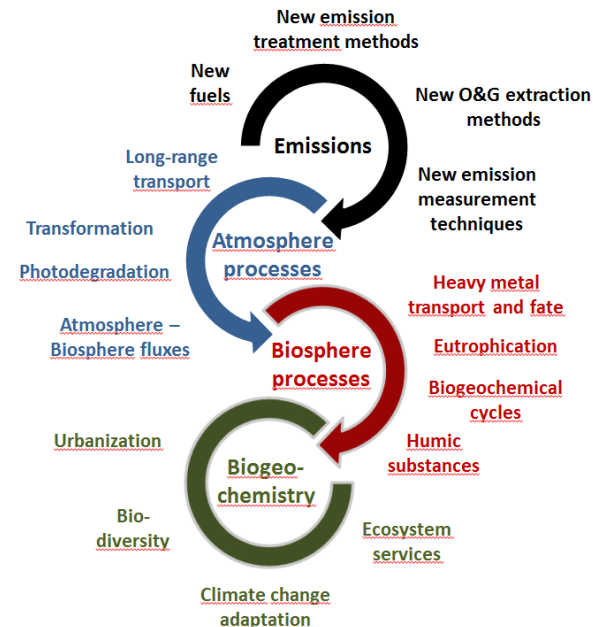


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Det matematisk-naturvitenskapelige fakultet

# Health, Safety and Environment (HSE)

KJM3070 Colloquium



# Safe Job Analysis (SJA)

- Safe job analysis must be made for all analytical operations **representing any danger**
  - What can go **wrong**?
  - What can we do to **avoid** this?
  - What can we do to **minimize** the damage?

## Risk assessment: CertoClav 12L Autoclave

What can go wrong	Possible Risk	What can be done to prevent accidents	What can be done to reduce the consequences if an accident should occur
Explosion due to very high pressure inside chamber (above 4,1 bars)*	Burns, blindness, and possible risk of death	<p>Work in the hood</p> <p>Wait enough time at the end of the experiment, so that the pressure has fallen to 0 bars and the temperature is below 80°C.</p> <p>Use gloves to take out the samples.</p> <p>Follow carefully the step by step procedure for operating the autoclave (instructions given on autoclave)</p>	<p>Leave the area if accident should occur &amp; contact safety inspector Vidar Blekestad, supervisor Rolf Vogt, Alexander Engebretsen or Christian W. Mohr.</p> <p>Place the burned area under cold water.</p>
Severe burns due to high temperatures ( $\approx 121^\circ\text{C}$ )	Burns	<p>Always consult an experienced user of the instrument for a demonstration before running the instrument for the first time.</p>	<p>If serious accident should occur contact ambulance and medical help (telephone no.: 113)</p>

\*The autoclave is setup with safety vents in order to avoid explosions. However the instrument must always be treated with the possibility of safety failure.

# Safety routines

- [HMS0504 – Feltsikkerhet](#)  
should have been taken before the fieldwork  
;-)
- [HMS0503 – Laboratoriesikkerhet](#)  
must be taken before the lab work
- In the lab you must use **goggles**
- The doors to chemicals must be **locked**
  - Door to lab must be **locked**
  - Cabinets must be **locked** and key hidden

# Health Safety and Environment

- All participants need to fill in field card form for participants
  - <https://nettskjema.no/a/130224#/page/1>
    - **Responsible of the field: Rolf D. Vogt**
    - **Project name or course number: KJM3070**
    - **Start/ Starting date of the field work: 23.10.2020**
    - **Finishing date of the field work: 23.10.2020**
- Participation is mandatory
  - though send me an e-mail and explain why if it is impossible within 2 days



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# Analysis plan



Colloquium, KJM3070

# Lab work

# Conductivity

- Conductivity meter
  - The instrument is calibrated using  $84 \mu\text{S}/\text{cm}$  calibration solutions
- The measurements are done for **quality control** purposes in order to compare measured and calculated conductivity
- Determined as described in ISO7888 using non-filtered water sample and preferably measured at  $25^\circ\text{C}$ .
- The reading is presented as  $\text{mS m}^{-1}$  ( $1\text{mS m}^{-1} = 10\mu\text{S}/\text{cm}$ )
- No SJA needed





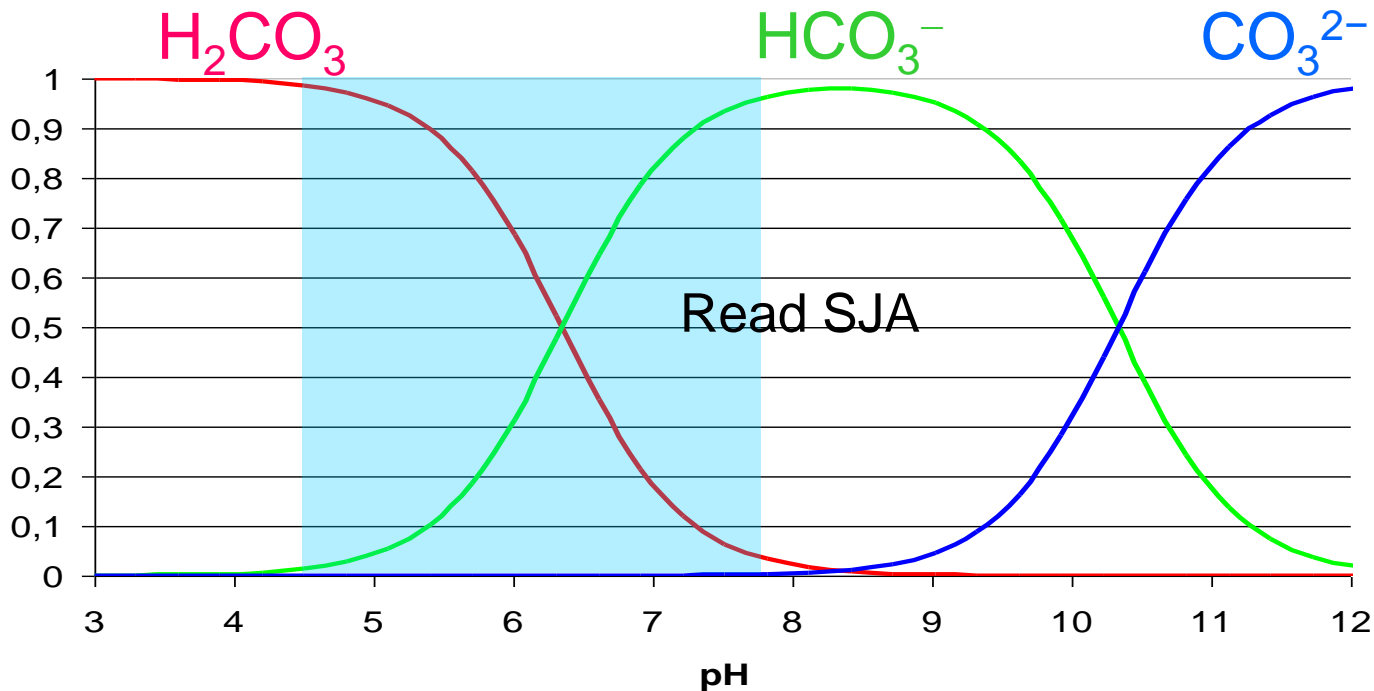
# {H<sup>+</sup>} determined using pH electrode

- Orion pH-meter with a Ross pH electrode
  - The pH-meter is calibrated with pH = 4.00 and 7.01 buffer solutions
- Risk of degassing of CO<sub>2</sub>
  - Stir till stable – wait till stable
- Determined as described in ISO10523 using non-filtered water sample
- Measurements should preferably be conducted at 25°C
- No SJA needed



# Total Alkalinity titration

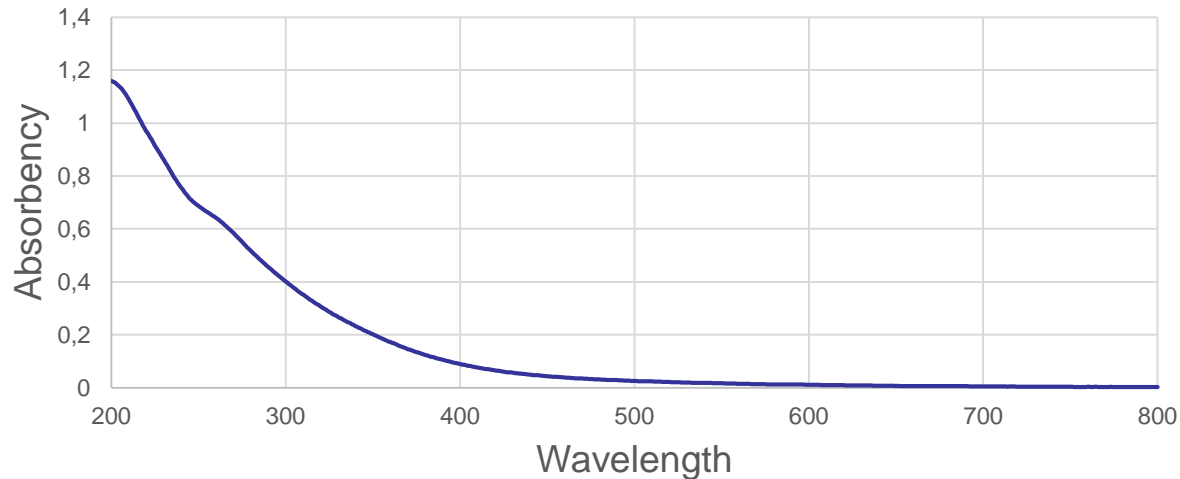
- Determined potentiometrically as described in ISO9963
  - Titration with acid to pH 4,5 and preferably measured at 25°C
- $$\text{CO}_3^{2-} + \text{HCO}_3^- + 3\text{H}_3\text{O}^+ \rightleftharpoons 2\text{H}_2\text{CO}_3 + 3\text{H}_2\text{O}$$
- Total alkalinity ( $=[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ ) +  $\text{H}^+$  needed to change the pH from sample pH down to pH 4.5 Endpoint in the acid range
  - Also other weak acids ( $\text{A}^-$ ,  $\text{Al}(\text{OH})_n^{3-n}$ )



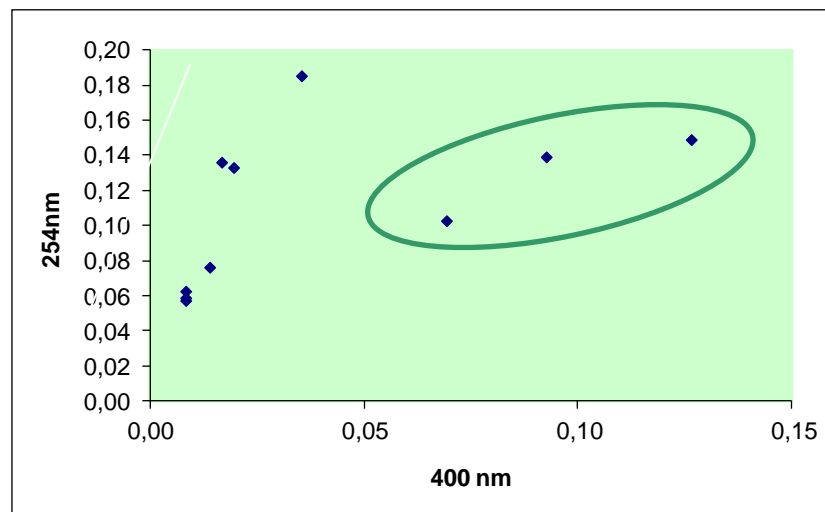
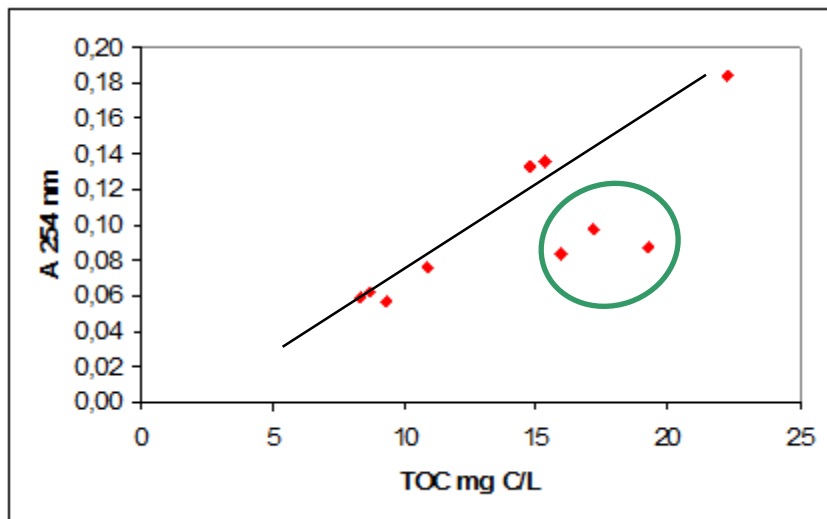
# UV-vis

- Measurement of absorbency scan and @  $\lambda$ 254, 400 and 600nm
- Absorbency at UV 254 nm is commonly used as a proxy for Dissolved Natural Organic Matter (DNOM)
  - Strongly correlated with TOC due to conjugated double bonds chromophores

Langtjern - absorbency



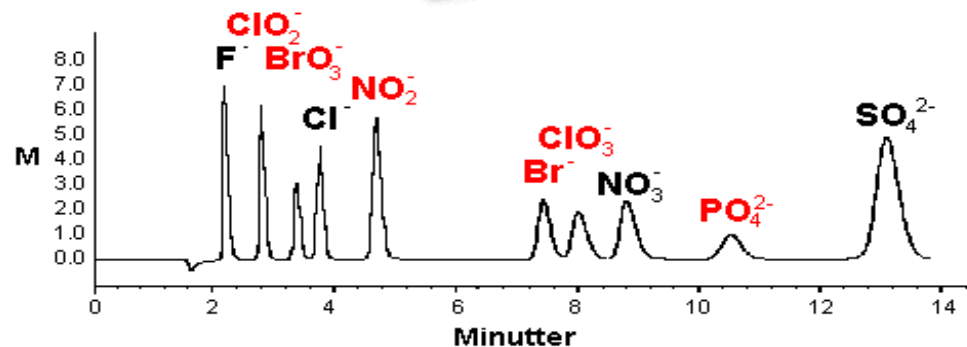
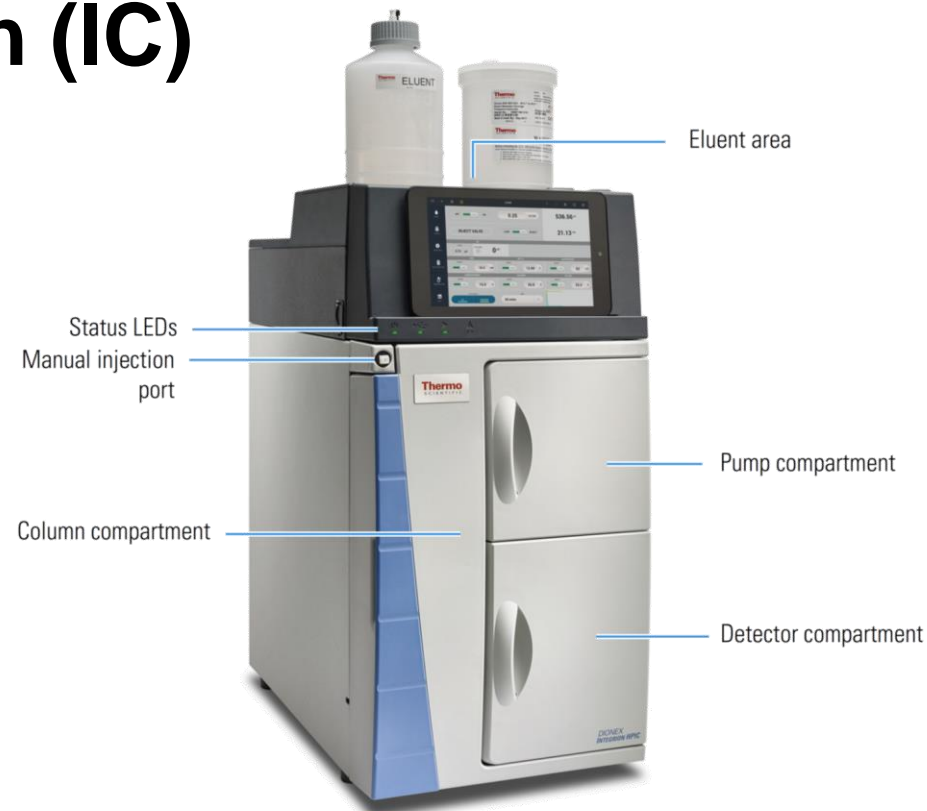
- Measurement of absorbency scan and @  $\lambda$ 254, 400 and 600nm
- Absorbency at UV 254 nm is commonly used as a proxy for Dissolved Natural Organic Matter (DNOM)
  - Strongly correlated with TOC due to conjugated double bonds chromophores
- Algae absorb light at UV 254 nm, but more than DNOM at VIS 400 nm
- Read SJA



# Analytical Instrument analysis

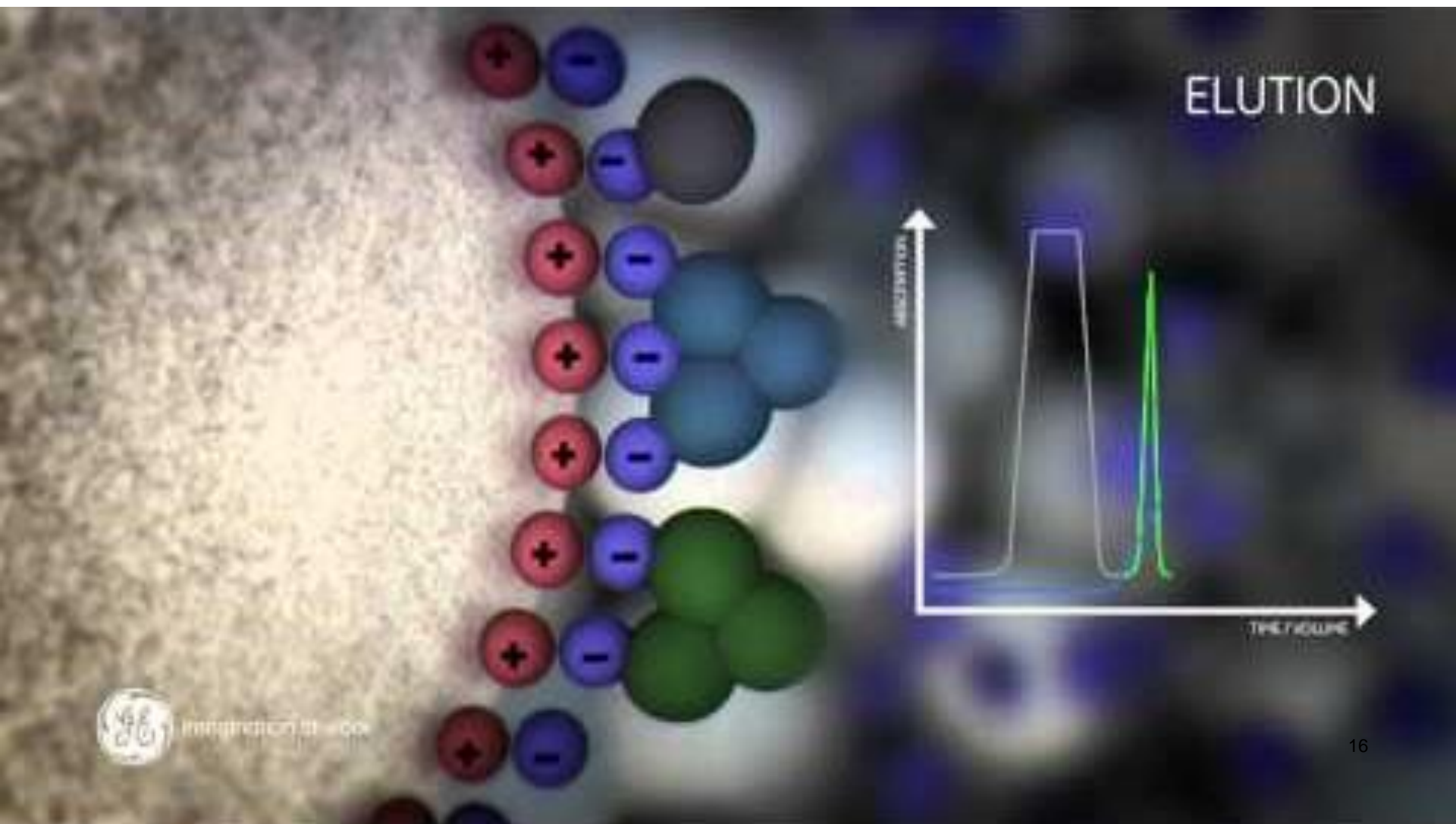
# Major anions to be determined by Ion Chromatograph (IC)

- Principle
  - The sample is injected in a flow of eluent
  - The analyte ions are separated by different degree of binding to the active sites on the ion exchange material
  - Cations are exchanged with  $H^+$
  - The activity x specific conductivity of the analyte along with  $H^+$  in the eluent stream are measured by means of a conductometer



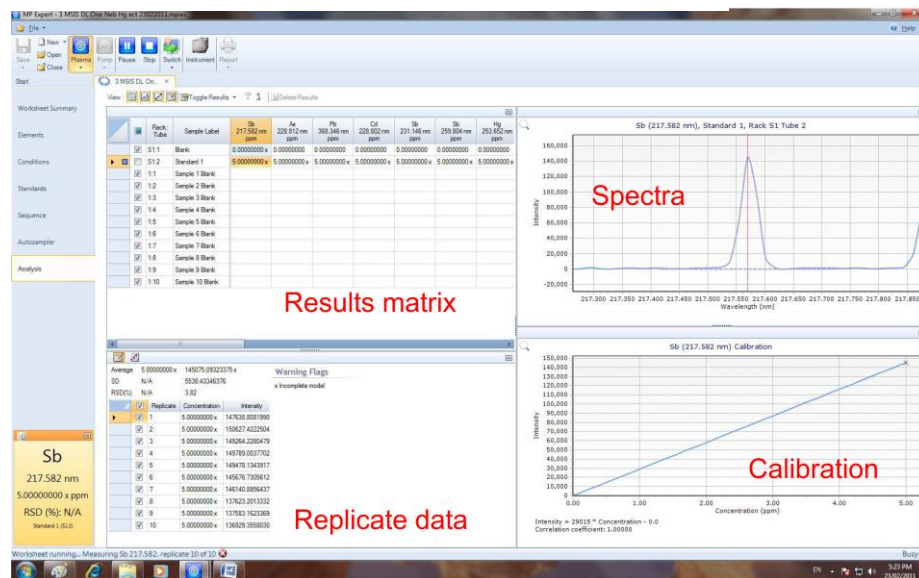
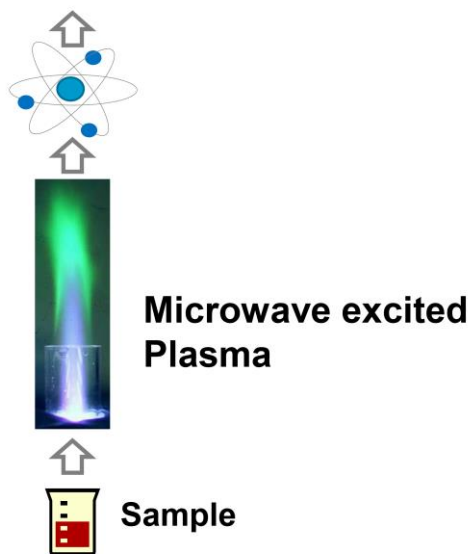
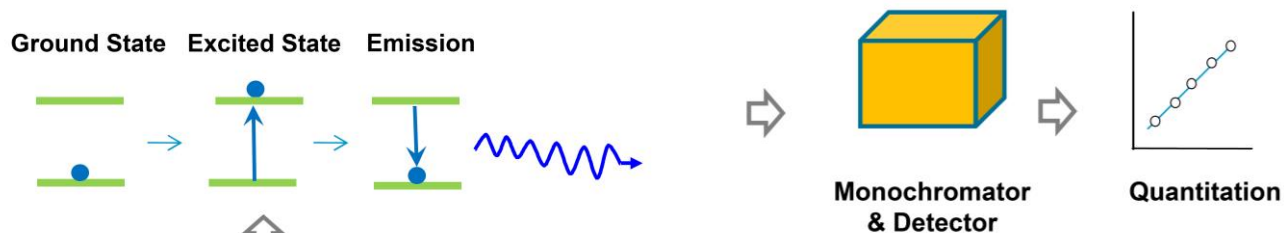
# Major anions to be determined by Ion Chromatograph (IC)

<https://www.youtube.com/watch?v=q3fMqgT1do8>



# Major cations to be determined by MP AES

= Microwave Plasma – Atomic Emission Spectrometer





# Major cations to be determined by MP-AES

<https://www.youtube.com/watch?v=sRwppw614aPg>, 0'59 to 3'22''



Agilent 4210 MP-AES

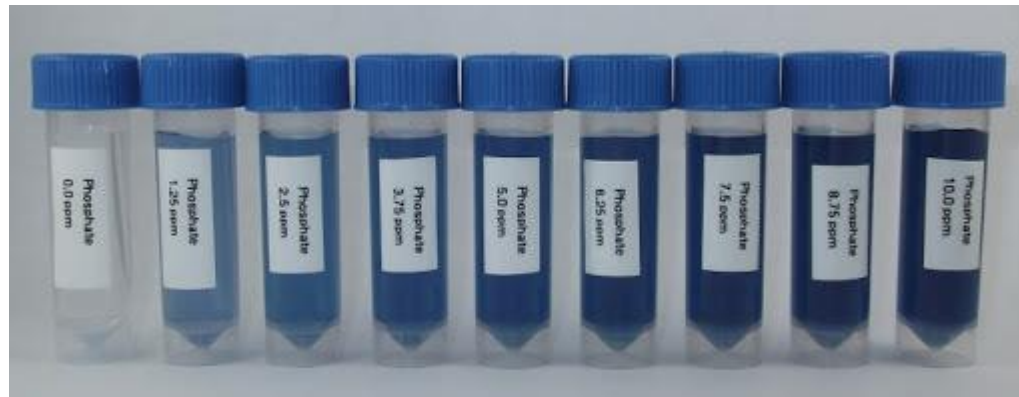
**THE SAFEST, MOST COST EFFECTIVE  
AND FLEXIBLE ELEMENTAL ANALYZER**



# External analysis

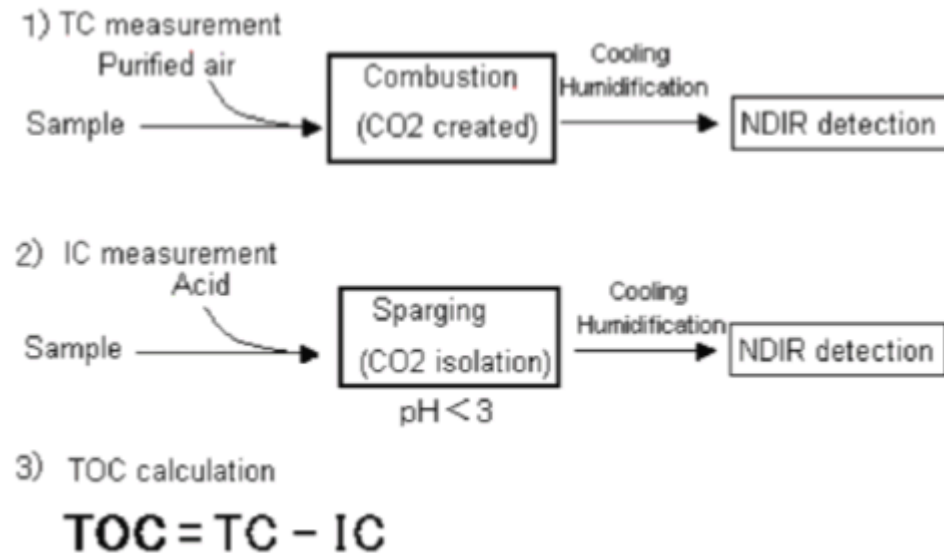
# P determination

- Orthophosphate reacts with ammoniummolybdate to a yellow-coloured phosphorousmolybdate acid, that is reduced with ascorbic acid in the presence of antimony to a strongly blue coloured complex
- This colour is measured photometrically as described in Norwegian Standard (NS 4724)



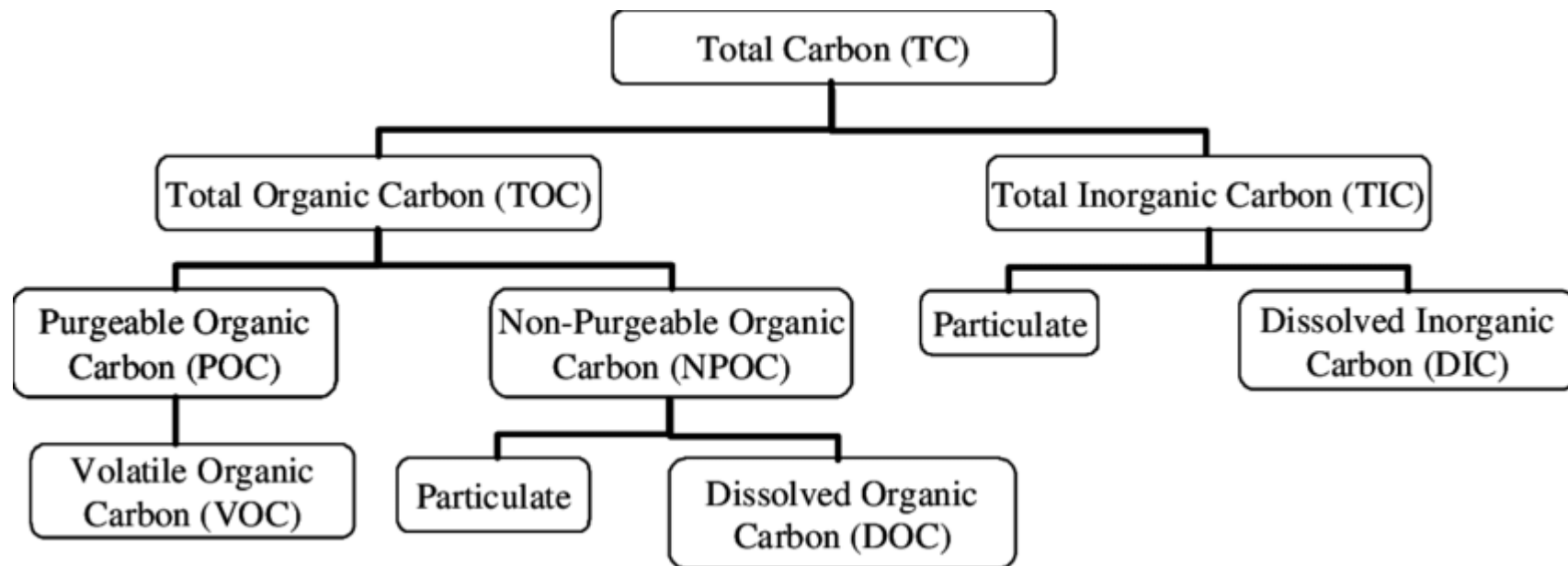
# Total organic carbon

- High temperature (680°C) catalytic combustion analysis on a Shimadzu TOC instrument
- Principle:
  - The organic carbon is combusted to **CO<sub>2</sub>** by high temperature and catalysis. The amount of CO<sub>2</sub> produced is measured using an **IR detector**



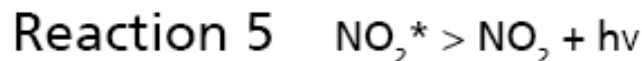
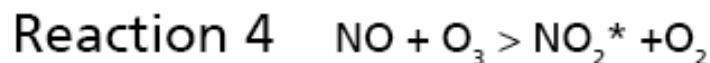
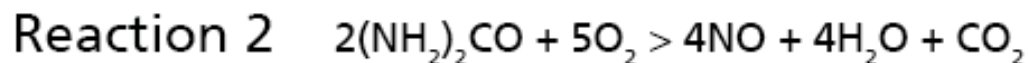
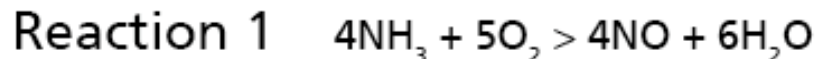
# Total organic carbon

- Analytes measured may include:



# Total nitrogen

- Total Nitrogen couples the Shimadzu TOC with a chemiluminescent nitrogen detector.
- The combustion tube is packed with a catalyst (platinum on an alumina support) and assembled in a furnace and heated to 720° C.

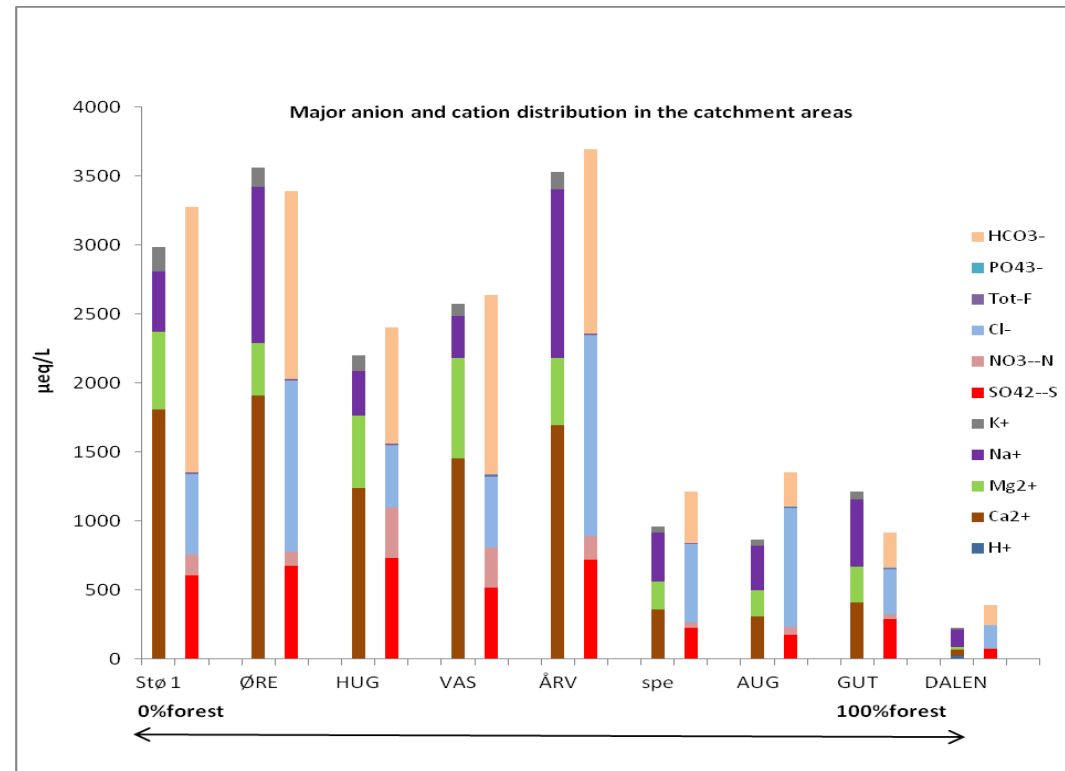


# Data assessment

# Problems with analysis of major anions and cations in water

- Anions are analysed in filtered raw water
- Cations are analysed in filtered water digested in acid ( $\text{HNO}_3$ )

- Colloidal material ( $<0.45\mu\text{m}$ ) is included in the cation analysis but not in the anion analysis







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**Species in natural freshwater**

**Central equilibriums in natural water samples**

**KJM3070**



# Compilation, calculations and QC of data

- After the analysis the data must be:
  - compiled
  - reckoned in terms of **equivalent charge** and
  - **quality controlled** by ion balance and agreement between measured and calculated conductivity

KJM307 2019 Colloquium Worksheet for water data.xlsx - Excel

	B	C	E	F	G	H	I	J	K	L
1			Sampling					Felt	Lab	
2	Log	Plot	Date/time	Volume	Comment	x-coordinate	y-coordinate	Cond <sub>25C</sub>	Cond <sub>25C</sub>	Temp.
3	Number	Letter	dd.mm.yy hh:mm	mL		N	E	µS.cm <sup>-1</sup>	µS.cm <sup>-1</sup>	°C
4		Nesøytjernet	20 okt. 19	2000	Kalkberggrunn	59°31'54	10°31'12			10,0
5		Lysakerelva	22 okt. 19	2000	Brunt vann	59°57.500'	10°37.406			10,0
6	1	Arungen	23 okt. 19	2000	Landbruk, brunt vann, høy turbiditet, høy vannføring	59°42'050	10°44'19	114		10,0
7	2	Gjersjøen	23 okt. 19	2000	Skogområde, brunt vann	59°45'294	10°46'439	103,0		10,7
8	3	Kolbotntjernet	23 okt. 19	2000	Algete og brunt vann	59°48'35	10°47'58	143		8,9
9	4	Sværsvann	23 okt. 19	2000	Brunt vann	59°49'041	10°53'225	20,3		7,2
10	5	Østensjøvann	23 okt. 19	2000	Næringsrik, mye fugl, kloakk	59°49'04	10°53'22	143		8,6
11	6	Solbergvannet	23 okt. 19	2000	Organisk jord, brunt vann	59°54'04	10°51'95	14,1		7,6
12	7	Lutvann	23 okt. 19	2000	Skog, lite nedbørsfelt, klart vann	59°55'19	10°52'62	24,9		9,7
13	8	Mandalsvannet	23 okt. 19	2000	Klart vann, råvannskilde	59°58'09	10°47'06	12,3		9,7
14	9	Akerselva	23 okt. 19	2000	Klart vann, Urbant	59°54'79	10°45'44	15,6		10,0

**EXAMPLE 1.3: Estimating the reliability of water analyses**

Your laboratory returns the following water analysis:

pH = 8.22

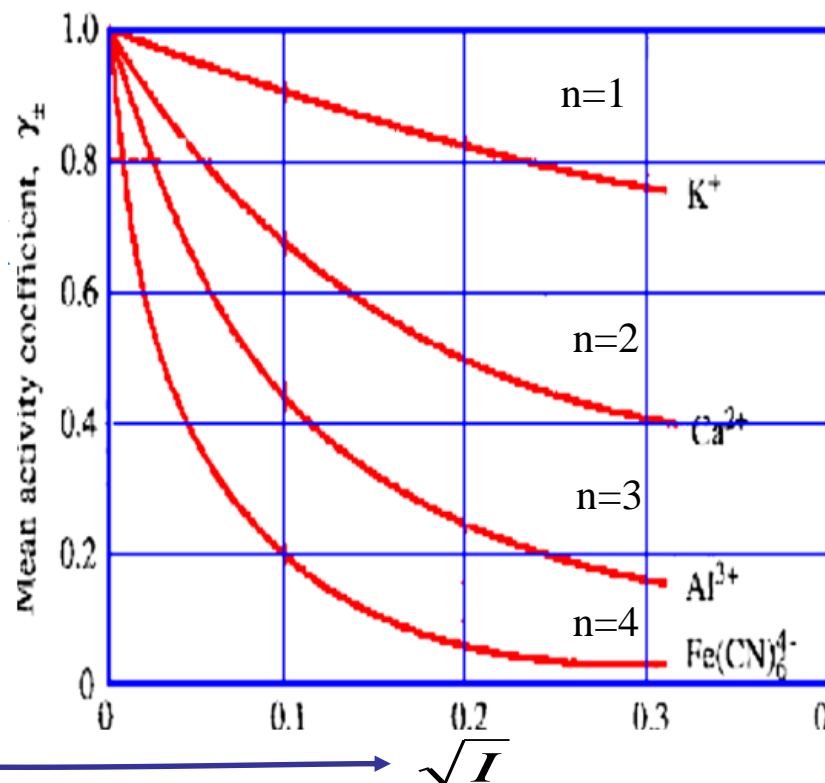
EC = 290  $\mu\text{S}/\text{cm}$

$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	
13.7	1.18	3.2	42.5	31.2	79.9	39	1.3	mg/l

Is this a reliable analysis?

# Activity

- $\{X\} = \gamma_X \cdot [X]$ 
  - $\{X\}$  is the activity to  $X$
  - $[X]$  is the concentration to  $X$
  - $\gamma_X$  is the activity coefficient to  $X$ 
    - $\gamma_X$  is dimensionless
    - It is determined by:
      - The diameter ( $\text{\AA}$ ) of the hydrated  $X$
      - Its valence ( $n_X$ )
      - The ionic strength ( $I$ )



- when  $I \rightarrow 0 \gamma \rightarrow 1$
- when  $I < 10^{-5} \text{M} \gamma \approx 1$

# Activity

$$I = \mu = \frac{1}{2}([A]n_A^2 + [B]n_B^2 + [C]n_C^2 + \dots) = \frac{1}{2}\sum [X]n_X^2$$

"I" is expressed in mol/L

Molar of the salt give rise to an I equals:

$$\text{AgCl:} \quad \frac{1}{2}(c \cdot 1^2 + c \cdot 1^2) = \frac{1}{2} \cdot 2c = 1c$$

$$\text{Ba(IO}_3)_2 : \quad \frac{1}{2}(c \cdot 2^2 + 2c \cdot 1^2) = \frac{1}{2} \cdot 6c = 3c$$

$$\text{BaSO}_4 : \quad \frac{1}{2}(c \cdot 2^2 + c \cdot 2^2) = \frac{1}{2} \cdot 8c = 4c$$

$$\text{Al(NO}_3)_3 : \quad \frac{1}{2}(c \cdot 3^2 + 3c \cdot 1^2) = \frac{1}{2} \cdot 12c = 6c$$

I can be roughly estimated based on the amount of solved material (TDS):

$$I = 2.5 \cdot 10^{-5} \cdot \text{TDS (mg/L)}$$

# Debye Huckel (DH) equation

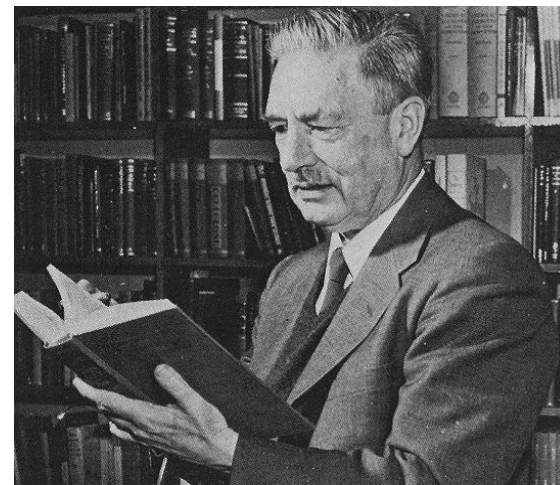
- For ionic strengths ( $I$ )  $< 0.1$  M the  $\gamma_x$  can be calculated by means of the e.g. *Debye Huckel* equation:

$$I < 0.1 \text{ M} \quad -\log \gamma_x = 0.5n_x^2 \cdot \frac{\sqrt{I}}{(1 + 0.33\overset{\circ}{a}_x \sqrt{I})}$$

$$I < 0.005 \text{ M} \quad (1 + 0.33\overset{\circ}{a}_x \sqrt{0.005}) \approx 1$$

$$-\log \gamma_x = 0.5n_x^2 \sqrt{I}$$

- 0.5 & 0.33 are temperature dependent table values
  - Presented values are for 25° C
- $\overset{\circ}{a}_x$  is a table value for the specie in question



Species	$\overset{\circ}{a}$
$\text{H}_3\text{O}^+$	9
$\text{Na}(\text{H}_2\text{O})_6^+$	4
$\text{K}(\text{H}_2\text{O})_6^+$	3
$\text{Cl}(\text{H}_2\text{O})_6^-$	3
$\text{Mg}(\text{H}_2\text{O})_6^{2+}$	8
$\text{Ca}(\text{H}_2\text{O})_6^{2+}$	6
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	6
$\text{Cu}(\text{H}_2\text{O})_4^+$	6
$\text{Zn}(\text{H}_2\text{O})_4^{2+}$	6
$\text{Pb}(\text{H}_2\text{O})_6^{2+}$	5
$\text{Al}(\text{H}_2\text{O})_6^{2+}$	9
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	9

# Calculated vs. Measured conductivity

- Calculate:

$\mu\text{M} \rightarrow \mu\text{eq/L}$

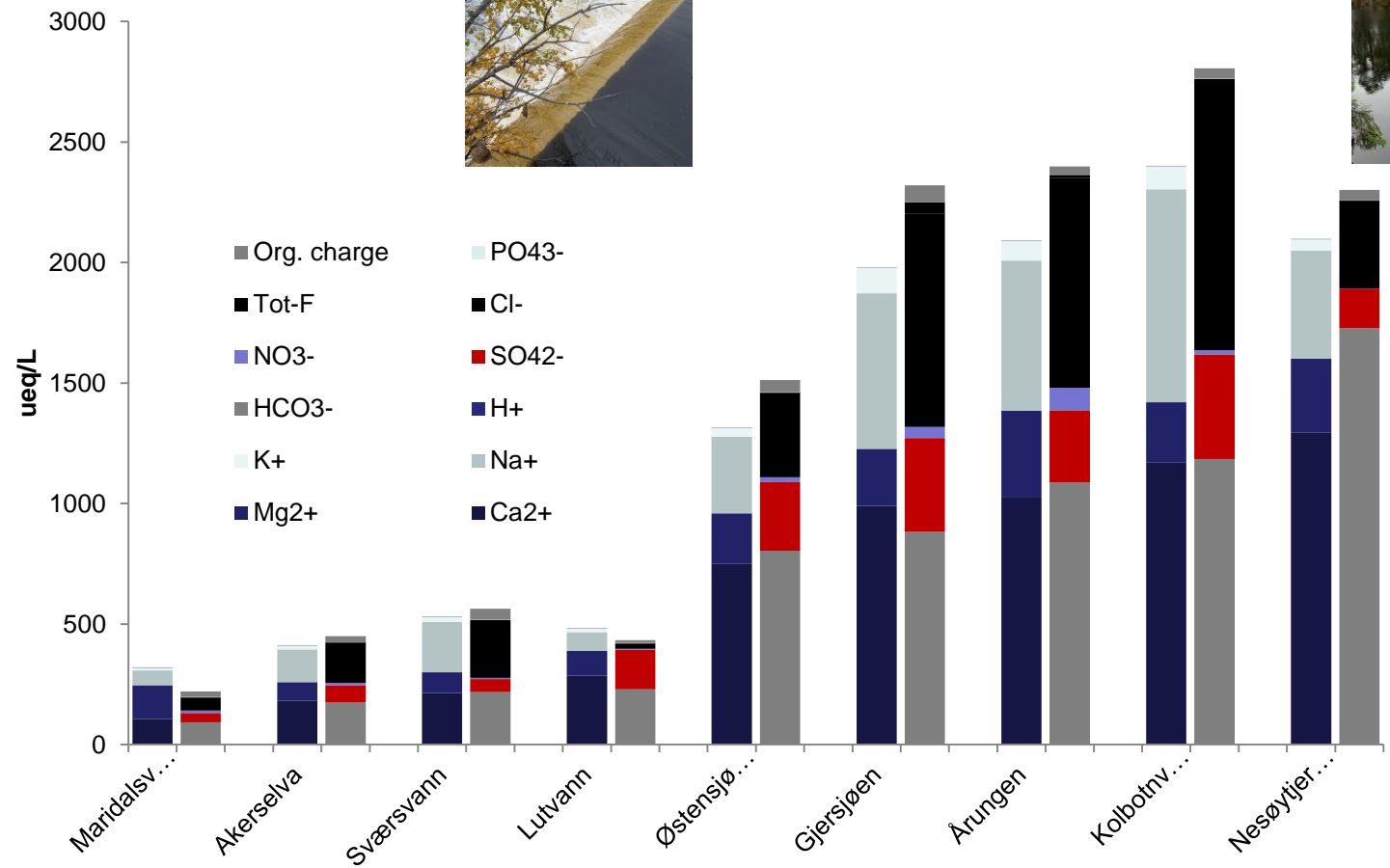
Ionic strength (I)

Activity {x}

Specific conductivity  $\rightarrow SC_X = \Lambda_m^0 \gamma_X m$

Add all the specific conductivities

Compare measured with specific conductivity

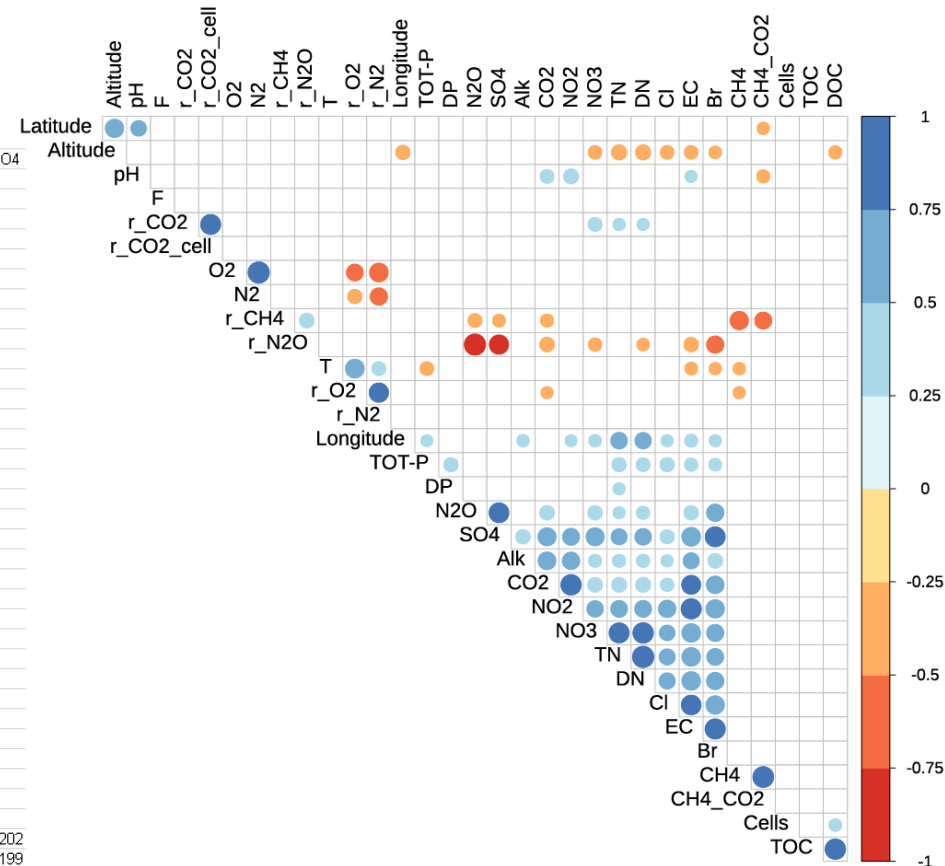




# Statistical analysis

- Correlation matrix
  - Identify parameters that are directly correlated or co-variate

	H+	sUVa	SAR	DOC	Ca2+	Mg2+	Na+	K+	SO42-	NO3-	Cl-	Free PO4
sUVa	0,806 0,000											
SAR	0,772 0,000	0,852 0,000										
DOC	0,842 0,000	0,867 0,000	0,953 0,000									
Ca2+	-0,301 0,052	-0,177 0,262	-0,046 0,774	-0,139 0,381								
Mg2+	-0,434 0,004	-0,344 0,026	-0,254 0,105	-0,322 0,038	0,934 0,000							
Na+	-0,265 0,090	-0,179 0,256	-0,062 0,698	-0,155 0,327	0,816 0,000	0,822 0,000						
K+	-0,234 0,136	-0,140 0,378	-0,031 0,845	-0,048 0,761	0,834 0,000	0,832 0,000	0,815 0,000					
SO42-	0,365 0,017	0,587 0,000	0,716 0,000	0,641 0,000	0,425 0,005	0,239 0,128	0,444 0,003	0,450 0,003				
NO3-	-0,246 0,116	-0,140 0,378	-0,143 0,366	-0,161 0,308	0,381 0,013	0,539 0,000	0,476 0,001	0,621 0,000	0,186 0,239			
Cl-	-0,456 0,002	-0,405 0,008	-0,316 0,041	-0,393 0,010	0,691 0,000	0,764 0,000	0,931 0,000	0,749 0,000	0,213 0,176	0,542 0,000		
Free PO4	0,356 0,021	0,647 0,000	0,576 0,000	0,479 0,001	0,047 0,770	-0,086 0,588	0,025 0,873	0,005 0,973	0,655 0,000	0,072 0,651	-0,186 0,238	
HCO3	-0,500 0,001	-0,445 0,003	-0,377 0,014	-0,431 0,004	0,841 0,000	0,846 0,000	0,608 0,000	0,607 0,000	0,023 0,883	0,222 0,158	0,600 0,000	-0,202 0,199

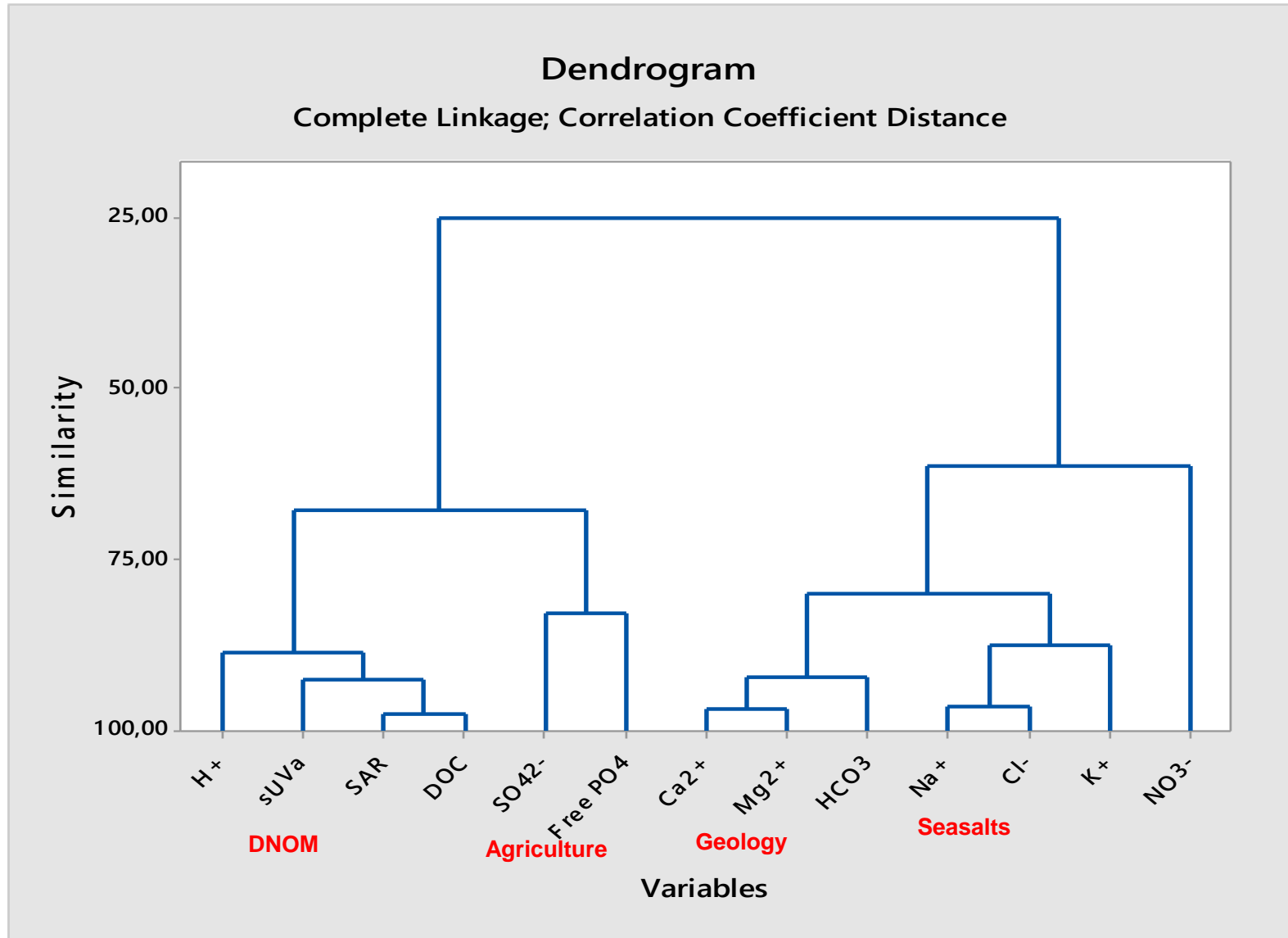




# Cluster analysis

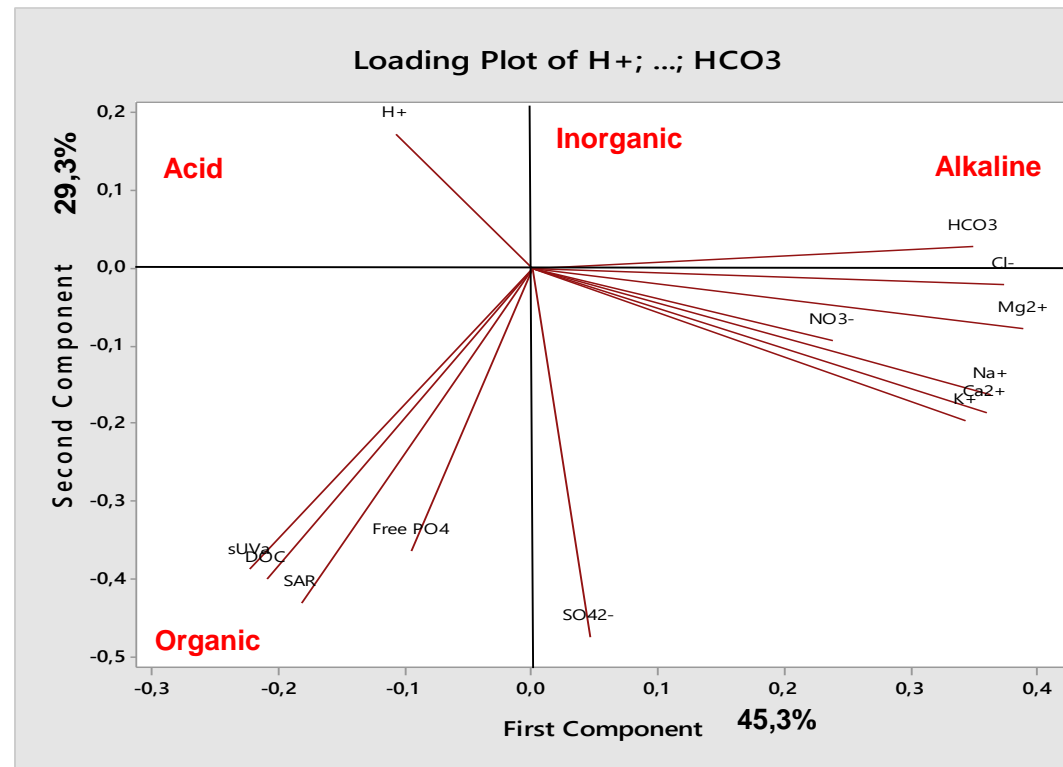
- Organizing parameters that co-variate in clusters
  - Identify
    - Links between parameters and groups of parameters
    - Identify key explanatory factors
    - General patterns

# Cluster analysis



# Principal Component Analysis

- Makes an n-dimensional graph of your n parameters
- Identifies the greatest variation in the swarm of data points and draws the PC1 through its axis.
- Identifies the next PC perpendicular to the previous
- Produce loading plots that are projections of the points to the PC plane



# Score Plot of H<sup>+</sup>; ...; DOP

