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Investigation of increased acid conductivity in water-steam circuits

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- Outline
  - Background and basics
  - Attacking the problem
  - QC of on-line monitors
  - Rules of thumb when observing
  - Ion chromatography at low µg/kg level
  - TOC/NVOC at µg/kg level
  - Examples
  - Conclusion

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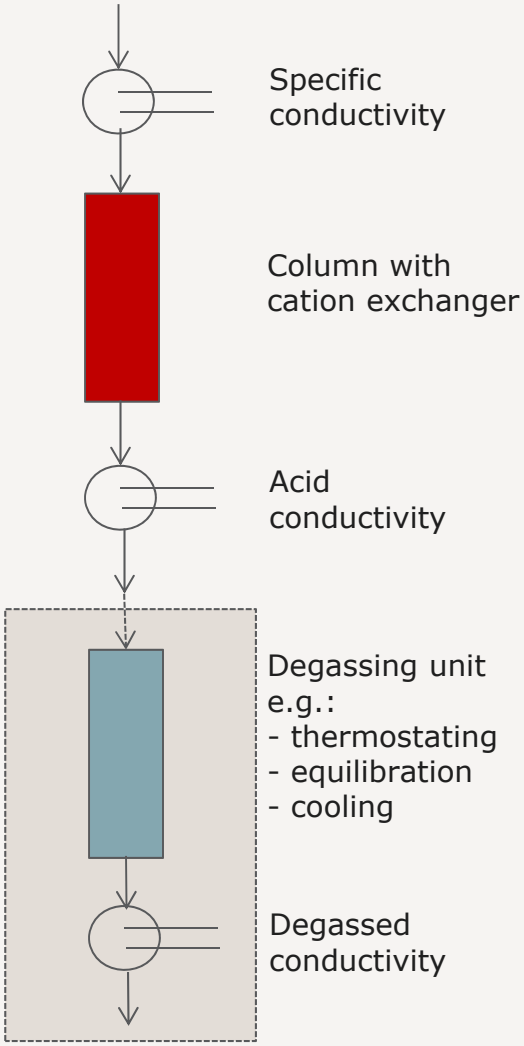
Conductivity basics



Term	Symbol	Comment
Specific conductivity Direct conductivity	SC	All ionic species contribute In pure water often used as measure of conditioning agent
Acid conductivity Cation conductivity Conductivity after cation exchanger	AC CC CACE	Contributions from conditioning agents like NH_3 and NaOH removed Contributions from salts amplified due to conversion to acid form Primary measure of purity of feed water and steam
Degassed conductivity Degassed cation conductivity	DC	Contributions from dissolved gasses (CO_2) removed CO_2 is a common contaminant, considered less harmful than salts and organic acid contaminants

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Acid conductivity - importance

- Acid conductivity is the most important parameter for supervision of purity of the water-steam cycle
- International guidelines use acid conductivity as key parameter for feed water and steam for
  - Phosphate treatment (PT)
  - Caustic treatment (CT)
  - All volatile treatment (AVT)
- and for boiler water for
  - Caustic treatment
  - All volatile treatment
- Typical specification for feed water and steam at action level 1 is 0.2 µS/cm

Feed water and water for steam attemperation Acid conductivity at AL1	
Conditioning	Spec. (µS/cm)
AVT, CT, PT	0.2

Steam Acid conductivity at AL1	
Without measurement of degassed conductivity	With measurement of degassed conductivity
Spec. (µS/cm)	Spec. (µS/cm)
0.2	AC: 0.5 DC: 0.2

Examples from VGB-S-010-T-00

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Acid conductivity – a non-specific measurement

Source of acid conductivity	Remark
Salts/acids with anions like chloride, sulphate …	Promotes corrosion in condensate and feed water trains, standstill corrosion and stress corrosion cracking in superheaters and turbine Sources: Primary and secondary cooling systems, water treatment plants …
Organic matter	Degrades in boiler, small organic acids like formic and acetic acid are formed and contribute to acid conductivity. The acids promote corrosion/stress corrosion cracking. Sources: Numerous, filter elements, surfaces, glycols in cooling water, organic conditioning agents
Carbon dioxide	Dissolves in water, carbonic acid is formed and contributes to acid conducitivity. Considered less harmful with respect to corrosion, but may mask other contamination. Sources: Air in-leakage, carbonates in conditioning chemicals (ammonia, sodium hydroxide)

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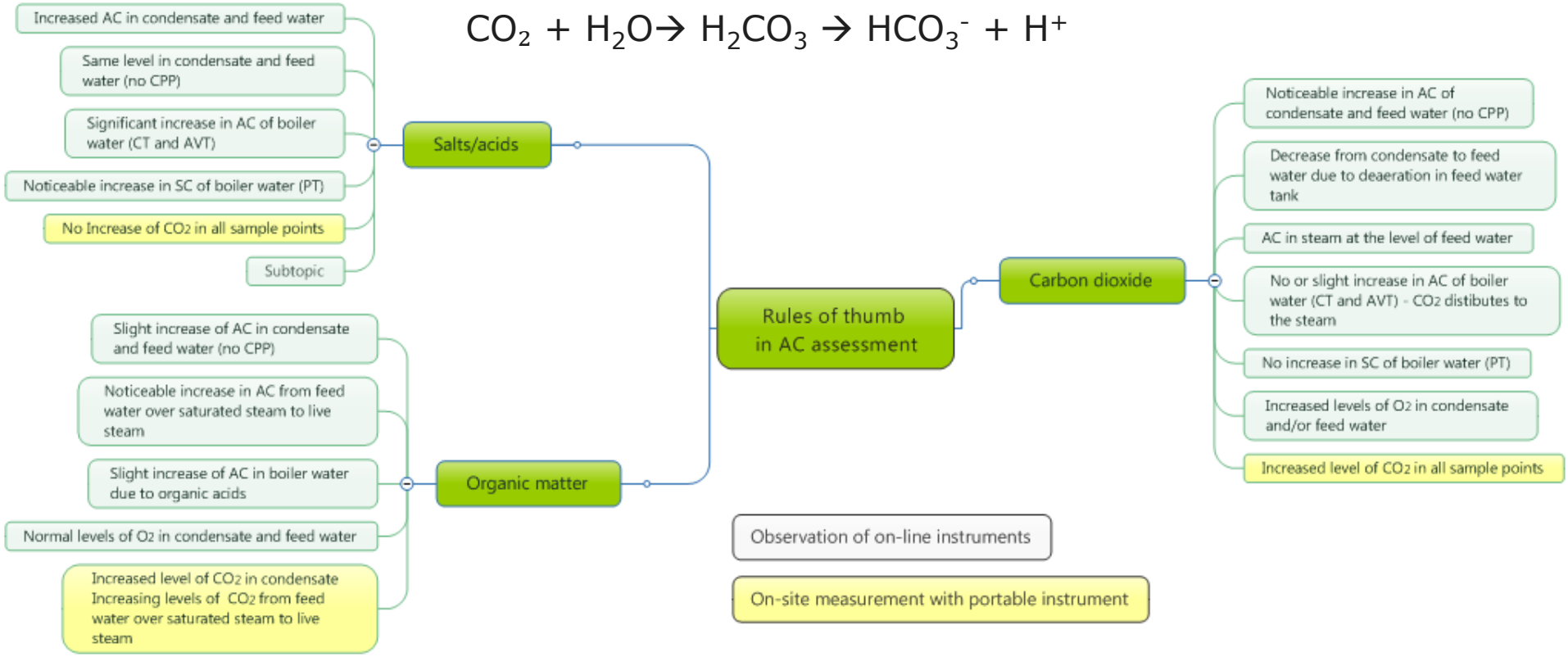
Handling the problem

Observation and common sense bring you far in assessment of increased acid conductivity

Organics → "$C_xH_yO_z$" + CH_3COOH + $HCOOH$ + CO_2 …
→ "$C_xH_yO_z$" + CH_3COO^- + $HCOO^-$ + HCO_3^- +$3H^+$ + …

"$C_xH_yO_z$" is small organic molecules

$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$



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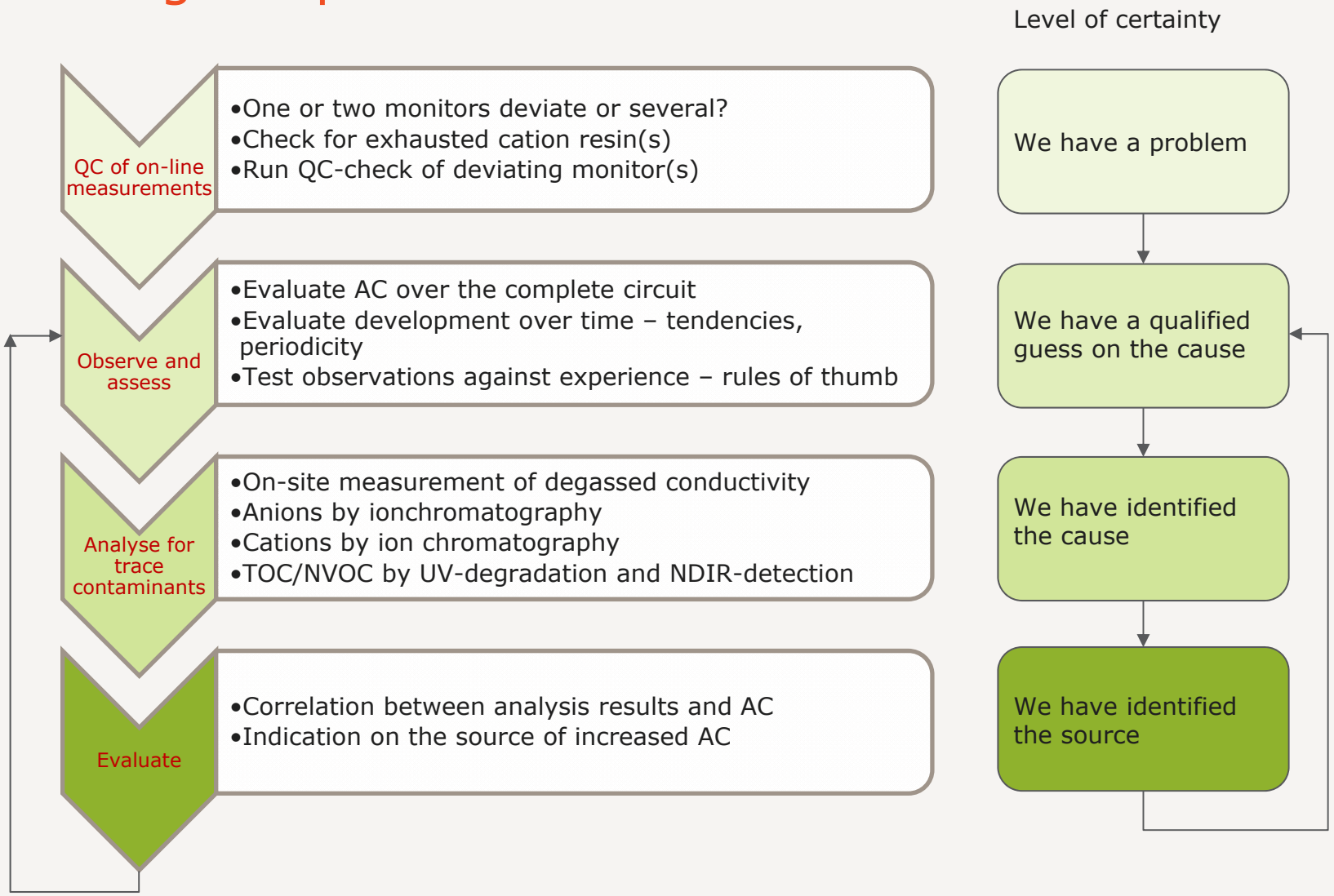
Attacking the problem



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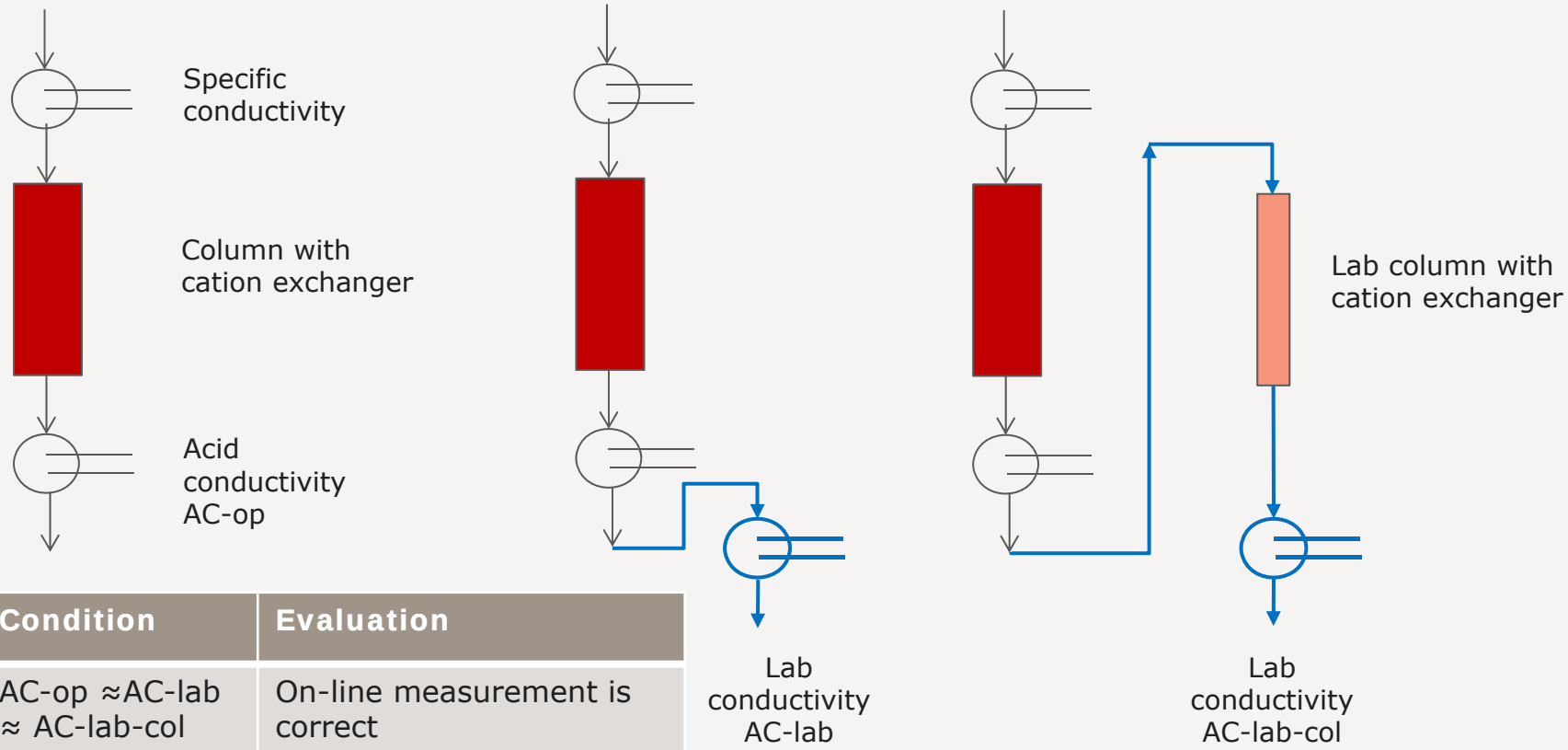
Handling the problem

QC of on-line measurement



Condition	Evaluation
AC-op ≈AC-lab ≈ AC-lab-col	On-line measurement is correct
AC-op ≈AC-lab > AC-lab-col	Malfunction of cation exchanger
AC-op >AC-lab ≈ AC-lab-col	Malfunction of conductivity meter

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Test of NJV3 condensate over a period

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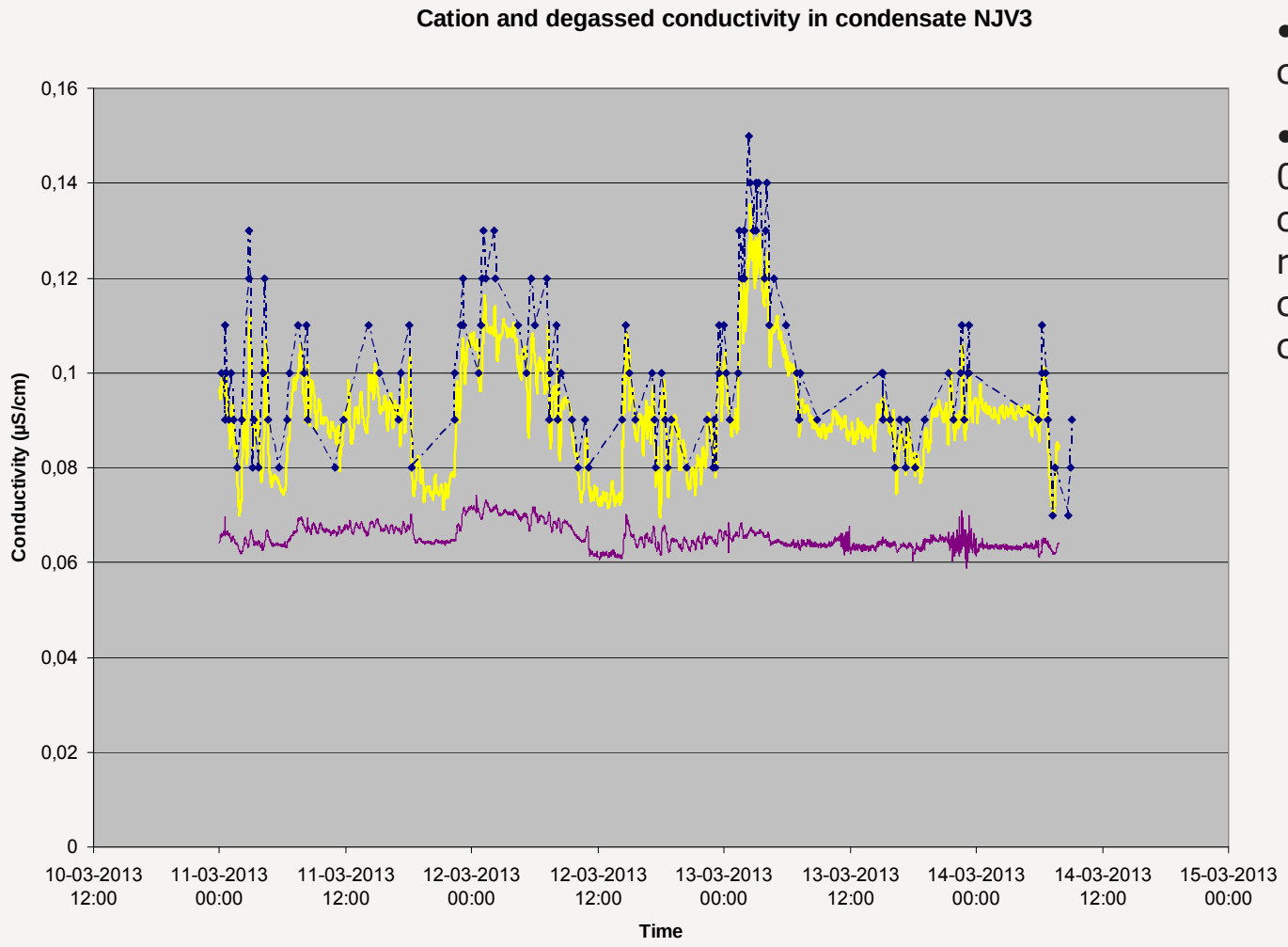
Source of AC in raw condensate?



Evaluation:

- AC-online and CC compares well
- DC remains below 0,07 µS/cm – traces of carbon dioxide responsible for the cation conductivity in condensate

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Ion chromatography at the low µg/kg level

Lab. facilities: Semi-clean room: Separate lab., air supply through filters, laminar flow bench for handling samples and standards

Equipment:	Dionex ICS-2000 (anions, gradient), Dionex ICS-1500 (cations, no gradient)
Eluent (generator)	Diluted KOH, 8-30 mM gradient, Diluted methanesulfonic acid, 20 mM
Columns:	IonPac AS15-5 um – 3x150 mm, IonPac AC12A-5 um – 3x150 mm
Injection vol:	1000 µL
Sampling:	Carefully rinsed sample bottles, pyrex glass for anions, HDPE for cations
Instructions:	Detailed instructions on sampling when samples are taken by others

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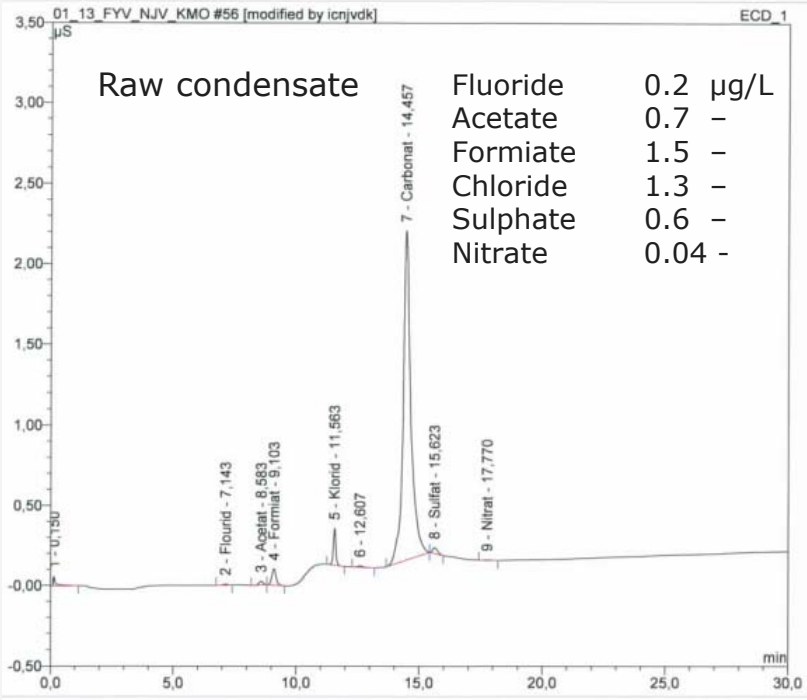
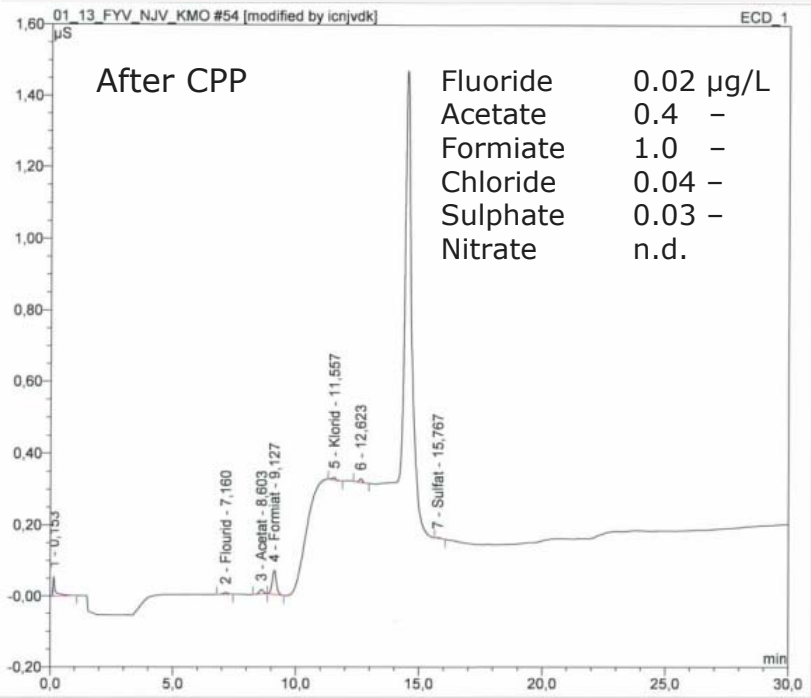
Anions at low level





Limit (µg/kg)	Fluoride	Acetate	Formiate	Chloride	Sulphate	Nitrate
DL	0.02	2.9	3.3	0.35	0.21	0.36
QL	1	5	5	1	1	1

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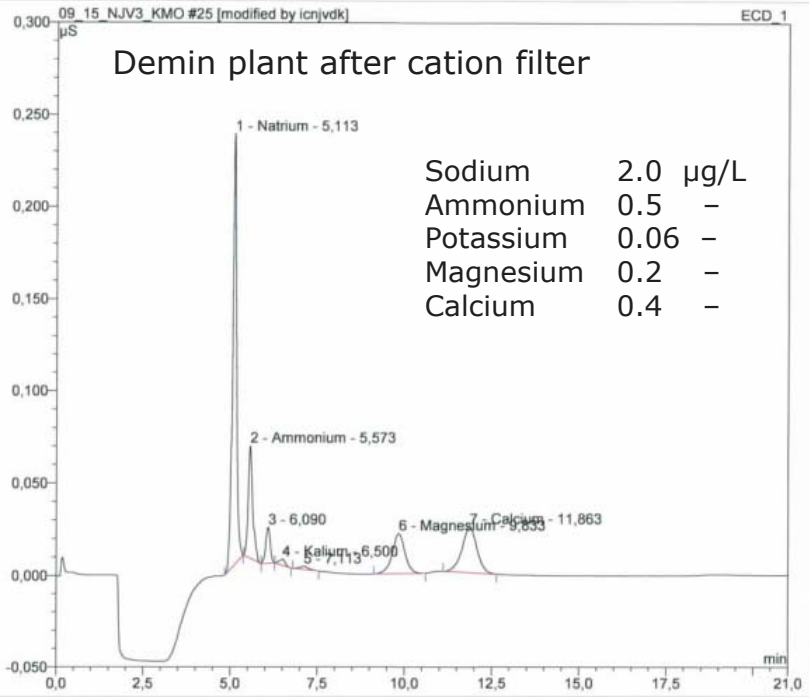
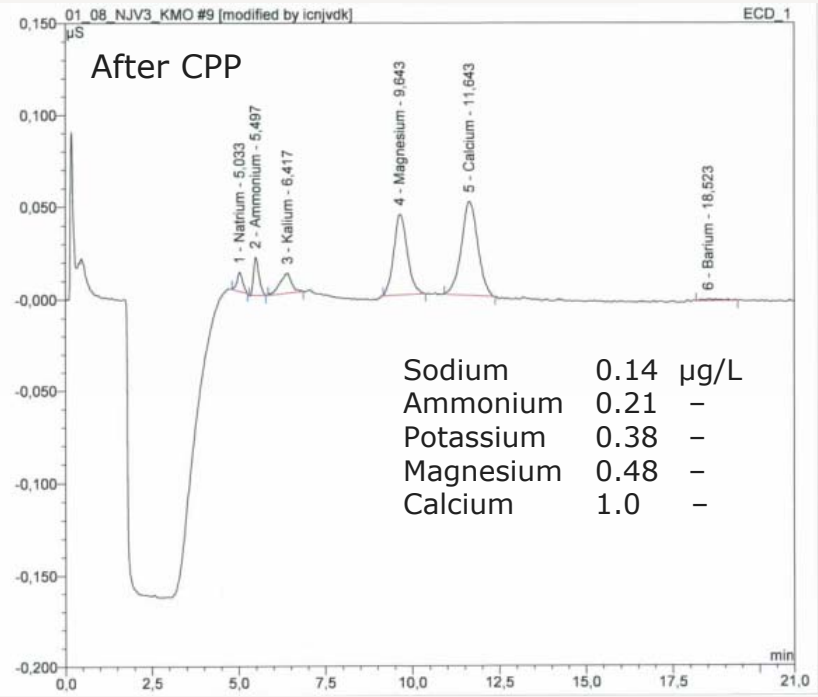
Cations at low level





Limit (µg/kg)	Sodium	Ammonium	Potassium	Magnesium	Calcium
DL	0.2	0.5	0.2	0.2	0.2
QL	1	2	1	2 (blind value ~1)	2 (blind value ~1)

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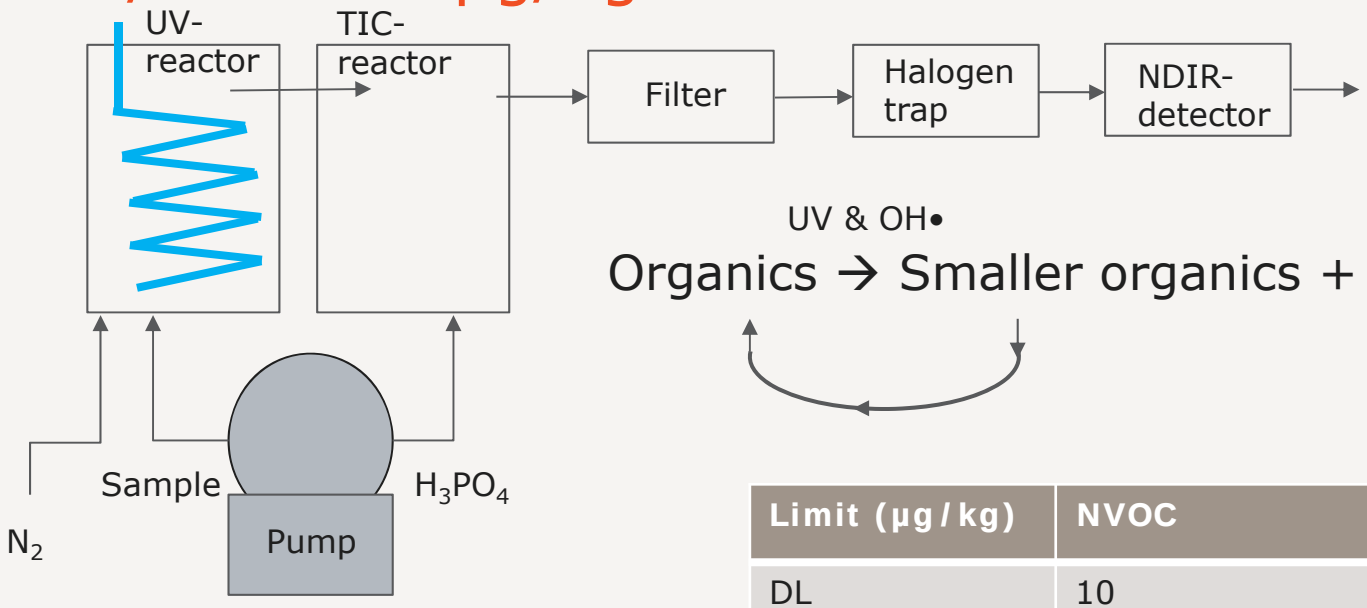
TOC/NVOC at µg/kg level



UV & OH•

Organics → Smaller organics + CO_2 + H_2O

Limit (µg/kg)	NVOC
DL	10
QL	40 (20 on 4 repetitions)

Lab. facilities: Water lab, air supply through filters
Instrument: Analytic Jena, Multi N/C UV HS TOC-analyser
Destruction mode: UV light alone, no oxidant added

Sampling: Carefully rinsed sample bottles, pyrex glass
Instructions: Detailed instructions on sampling when samples are taken by others

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Real life situation from Swedish CHP, conditioning: CT

Sample	AC online µS/cm	O_2 online µg/kg	SiO_2 online µg/kg	Na online µg/kg	Na lab µg/kg	
Feed water		9	14		64	
Boiler water	14.8					
Sat. steam	0.36		10			
Conden-sate	0,74	20		78		

Conclusion: Clear signs of condenser leakage!

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Real life situation from the same plant

Sample	AC lab µS/cm	DC lab µS/cm	O_2 online µg/kg	SiO_2 online µg/kg	Na lab µg/kg	Cl lab µg/kg
Feed water	0.243	0.091	8	1	<1	<2
Boiler water	0.633					
Sat. steam	0.250	0.095		2	<1	<2
Conden-sate	0.304	0.093	4		<1	<2

Conclusion: Acid conductivity caused by carbon dioxide – but no sign of air in-leakage. Uptake of carbon dioxide in ammonia stock solution is the likely source.

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Conditioning with DEHA – N,N-diethylhydroxylamine

- Described as conditioning agent for utilities and paper/pulp boilers in mid-1980 ties
- Effects claimed:
  - Passivation of steel surfaces
  - Rapid reaction with oxygen
  - Alkalising agent due to amines
  - Acetic acid as breakdown product – low amounts and acidic effect is neglicible and neutralised by amines
- Dosing:
  - Suitable pH and oxygen concentrations may be achieved by DEHA only

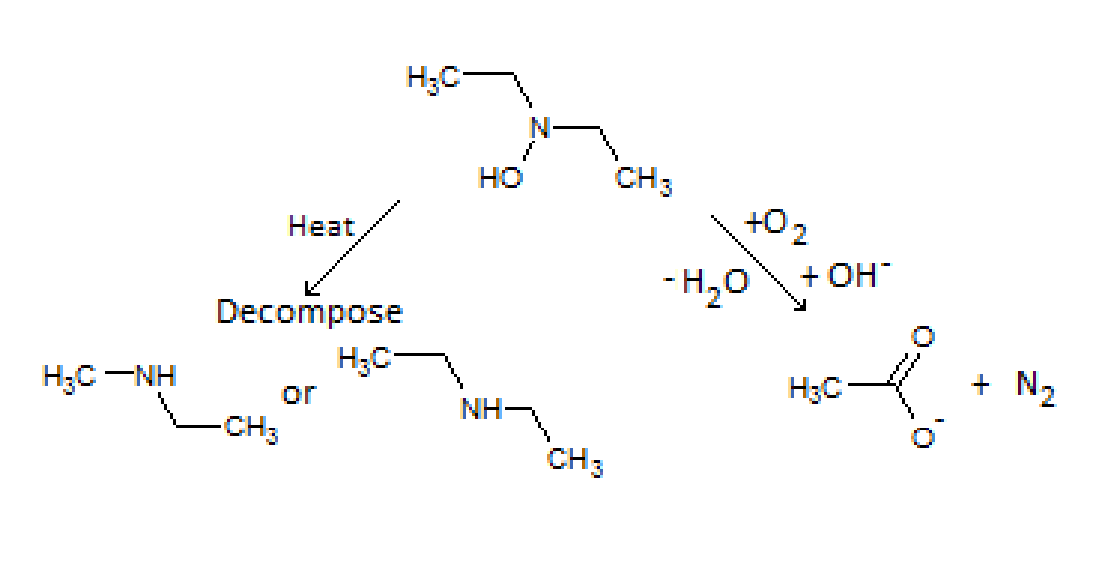
Ref. www.awt.org/certification/quiz4.pdf

Reaction with oxygen:

$4\ (C_2H_5)_2NOH + 9\ O_2 \rightarrow 8\ CH_3COOH + 2\ N_2 + 6\ H_2O$

Decomposes, when heated, to amines:

- diethylamine and methyl-ethyl-amine



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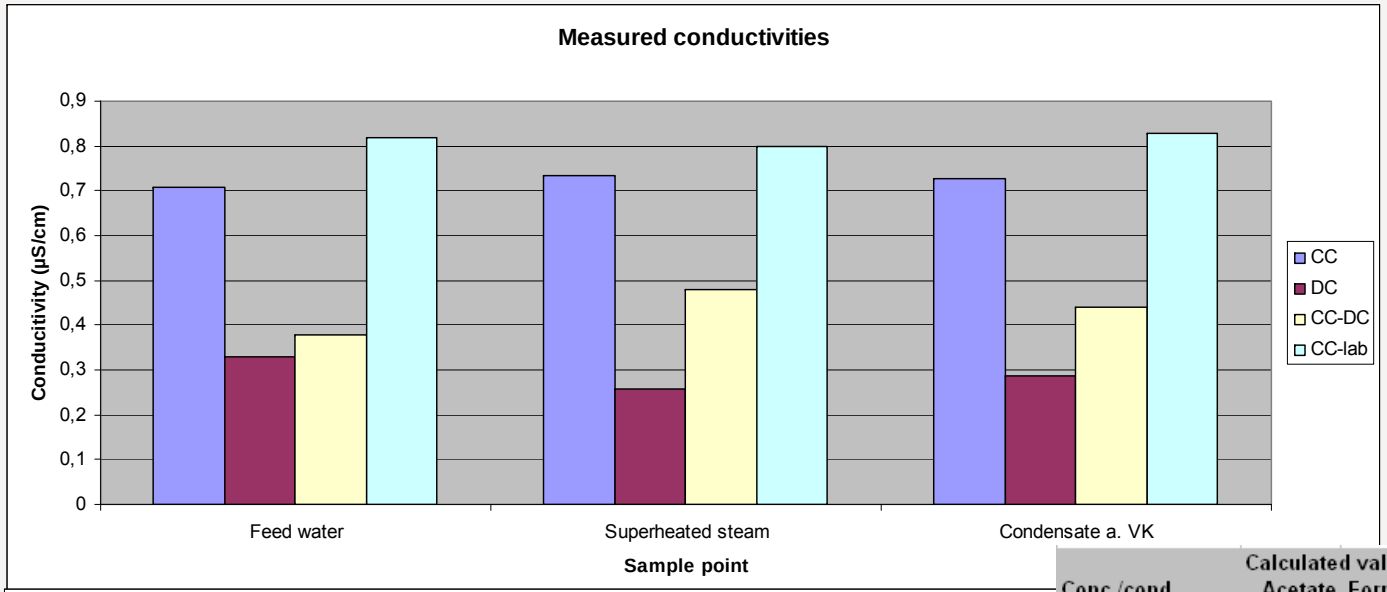
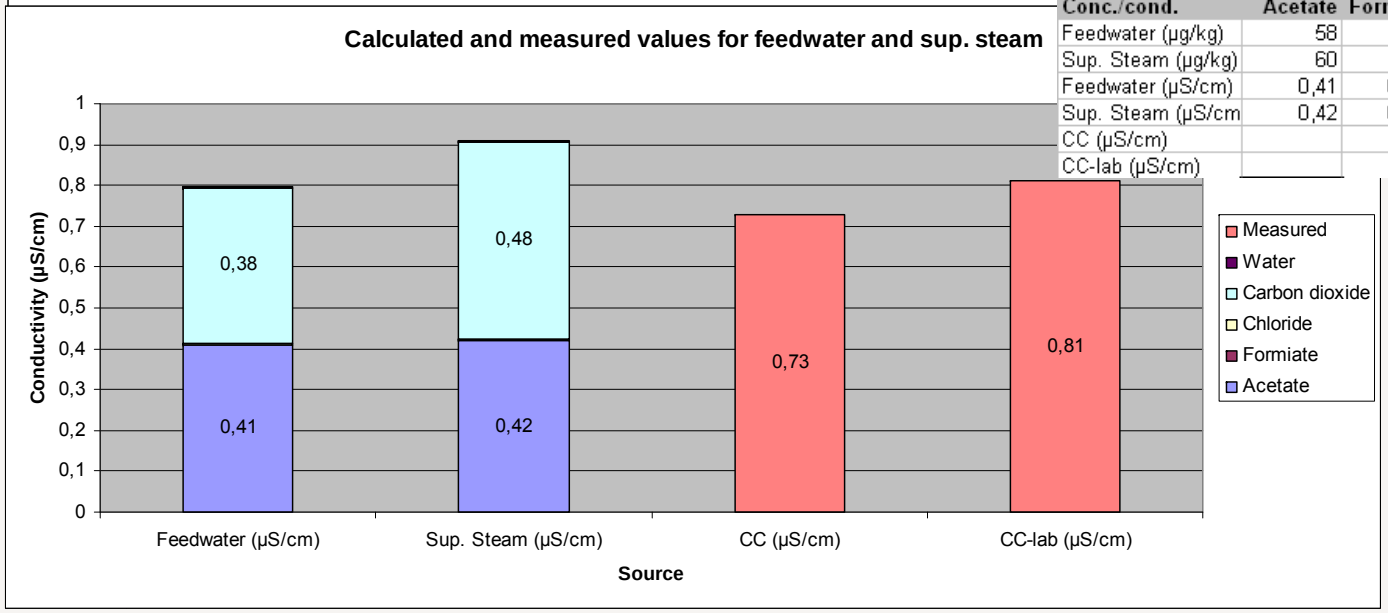
Explanation of acid conductivity



Comparison of measured vaues with the Swan Deltacon and lab measurements at different sampling points

	Calculated values (conc. in µg/kg, conducitivity in µS/cm)					
Conc./cond.	Acetate	Formiate	Chloride	Carb.dioxide	Water	Measured
Feedwater (µg/kg)	58	1	1	180		
Sup. Steam (µg/kg)	60	2	1	240		
Feedwater (µS/cm)	0,41	0,001	0,002	0,38	0,005	
Sup. Steam (µS/cm	0,42	0,002	0,002	0,48	0,005	
CC (µS/cm)						0,73
CC-lab (µS/cm)						0,81



Comparison of calculated values – from the IC analysis and the difference CC-DC – with the measured values in feedwater and superheated steam. It is evident that the CC is explained by acetic acid and carbon dioxide with about equal contributions

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Conclusions

- Acid conductivity is the most important and mostly used surveillance of purity in water-steam circuits.
- It is non-specific, i.e. there is no indication of what the cause of increased values is.
- The chemist should evaluate an excursion in a structured way:
  - Check the basics, QC of deviating measurement(s)
  - Observe chemistry measurements around the circuit
  - Evaluate using rules of thumb and experience
  - Measure degassed conductivity on-site
  - Analyse samples for trace contaminants
  - Some or all of these tools lead to the source of increased acid conductivity
- This approach has shown its value both at local plants and at distant CPH's that COWI/Nordjyllandsværket's lab serve.

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