Degassed conductivity – some experiences

SIAPWS general meeting, Malmö, March 2013

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21 March 2013

(Data Sheet No. DenA23481XX0)

Degassed Cation Conductivity

First test at the local unit – NJV3

Initial test of Swan Deltacon

Date	Sampling point	Kemotron/On-line meas		SWAN			Flow	IC-analysis anions (ppb)				IC-analysis cations (ppb)			
		SC	CC	SC	CC	DC	L/h	Acetate	Formiate	Chloride	Sulphate	Sodium	Ammonium	Potassium	Calcium
20-10-2011	Lab. Deionate	0,640	0,740	0,640	0,800	0,150	7,2								
24-10-2011	same			0,388	0,556	0,155	7,0	<2	<2	<2	<2	<1	21	<1	1
26-10-2011	NJV3 Condensate	1,470	0,073	1,490	0,122	0,111	10,0	<2	2,2	<2	n.d.	<1	230	n.d.	1,1
27-10-2011	NJV3 feedwater	1,720	0,078	1,680	0,144	0,113	10,0	<2	3	<2	n.d.	1	240	n.d.	2,5
08-11-2011	NJV3 Eft. KR.-Anl.	0,054	0,054	0,055	0,087	0,116	6,0	SWAN attached with coated aluminium tube (Oxyguard oxygen monitor)							
	same	0,054	0,054	0,055	0,069	0,087	11,0								
	same	0,054	0,054	0,054	0,067	0,083	12,0								
	same	0,054	0,054	0,055	0,061	0,074	15,0								
09-11-2011	same	0,054	0,054	0,056	0,073	0,079	11,0	SWAN attached with 130 cm TYGON tube							
17-11-2011	NJV3 feedwater	7,760	1,310	7,550	1,250	0,337	13,0	<2	<2	<2	<2	<1			
18-11-2011	same			7,540	1,230	0,237	9,0	n.d.	4,3	2,1	<2	1		n.d.	n.d.

Conductivities in µS/cm
Temp. comp. SC = Ammonia, CC & DC = Acid

Evaluation:

- Initial tests on pure water showed too high results for CC and DC compared to stationary monitors
- Tubing was not the cause, rather the cation exchanger delivered with the instrument
- After change to the standard quality used for cation filters at NJV, the results matched the on-line monitors

Confidentiality - None (C1)

Test at Swedish CHP's – Plant 1

Analyser attached to superheated steam sampling point at approximately 14:00								
Sample point	**Time**	**SC-lab**	**SC-online**	**CC-lab**	**CC-online**	**SC**	**CC**	**DC**
SatSteam	14-15	7,6	7,04	0,364	0,358			
SupSteam	ca. 14:30					7,42	0,482	0,152
	14:55					7,46	0,493	0,147
Analyser attached to condensate after VK1+VK2 at 14:56								
Cond VK	14-15	6,95	6,56					
Cond LFV	14-15	6,85	6,71	0,44	0,423			
Cond VK	15:10					6,88	0,523	0,147
	15:38					7,04	0,511	0,137

Evaluation:

- This plant has experienced air in-leakage around the condensers quite often – test on-site with the Deltacon analyser
- Comparison with on-line instrumentation and lab. equipment still a bit off
- Conclusion is that carbon dioxide is mainly responsible for the cation conductivity – confirmed by IC analysis
- Flow to analyser around 6 L/h – too low to get values consistent with on-line or lab equipment

Confidentiality - None (C1)

Test at Swedish CHP's – Plant 2

Sample point	Time	SC-lab	SC-online	CC-lab	CC-online	SC	CC	DC	
Feedwater	9:30-10:30	5,4	5,16	0,092	0,08				
SatSteam	9:30-10:30			0,099	0,097				
SupSteam	9:30-10:30			0,125	0,127				
Cond	9:30-10:30			0,091	0,096				
Cond	10:30				0,095	4,71	0,175	0,105	
	10:35				0,094	4,7	0,162	0,105	
	10:48				0,096				
	10:51				0,096				
	10:58				0,04				
SupSteam	10:43				0,092	5,23	0,181	0,104	
	10:49				0,093	5,22	0,306	0,117	
	10:52				0,093	5,21	0,33	0,14	Disrupted, temp. > 40 deg.
SatSteam	11:05				0,087	5,08	0,253	0,247	
	11:08				0,085	5,12	0,194	0,208	
	11:11				0,085	5,09	0,184	0,174	
	11:15				0,086	5,09	0,177	0,135	
	11:18				0,086	5,08	0,171	0,118	
	11:20				0,086	5,1	0,168	0,109	
	11:30			0,086					
	12:25			0,09	0,086				
Feedwater	11:06			0,078	0,07				
	11:09			0,077	0,07				
	11:19			0,077	0,069				
	12:32					4,98	0,147	0,111	
	13:50		4,99		0,064	5,01	0,15	0,105	
	14:18		4,79			4,86	0,141	0,102	
	14:50		4,63			4,7	0,146	0,104	

Evaluation:

- This plant has better water chemistry and usually very low CC
- The analyser compares poorly with the on-line and lab. Instruments
- Flow around 6 L/h – too low for high purity water, must be > 10 L/h (my misunderstanding!)

Confidentiality - None (C1)

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Test at NJV3 condensate over a period

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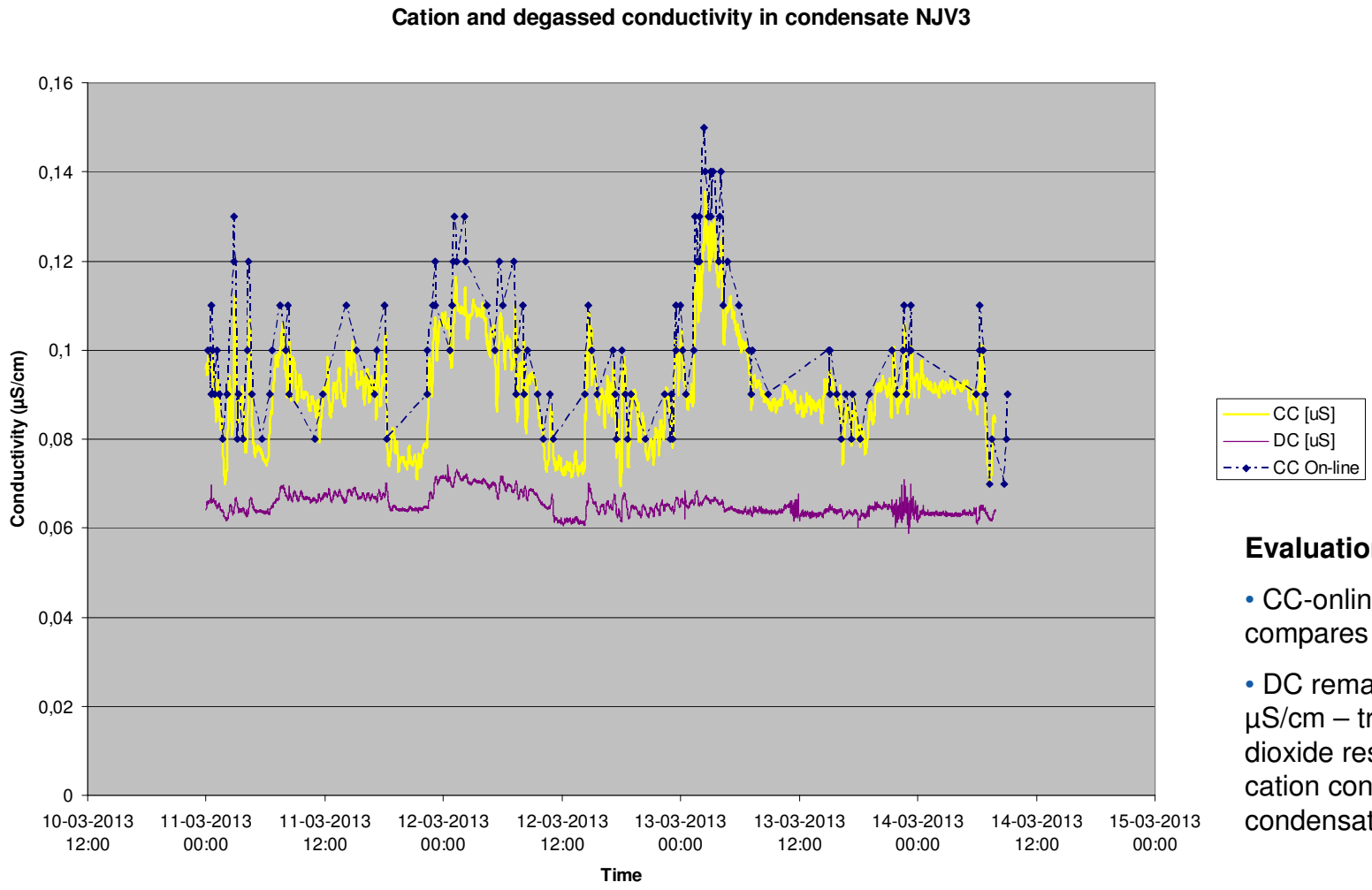
Source of CC in raw condensate?



Evaluation:

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

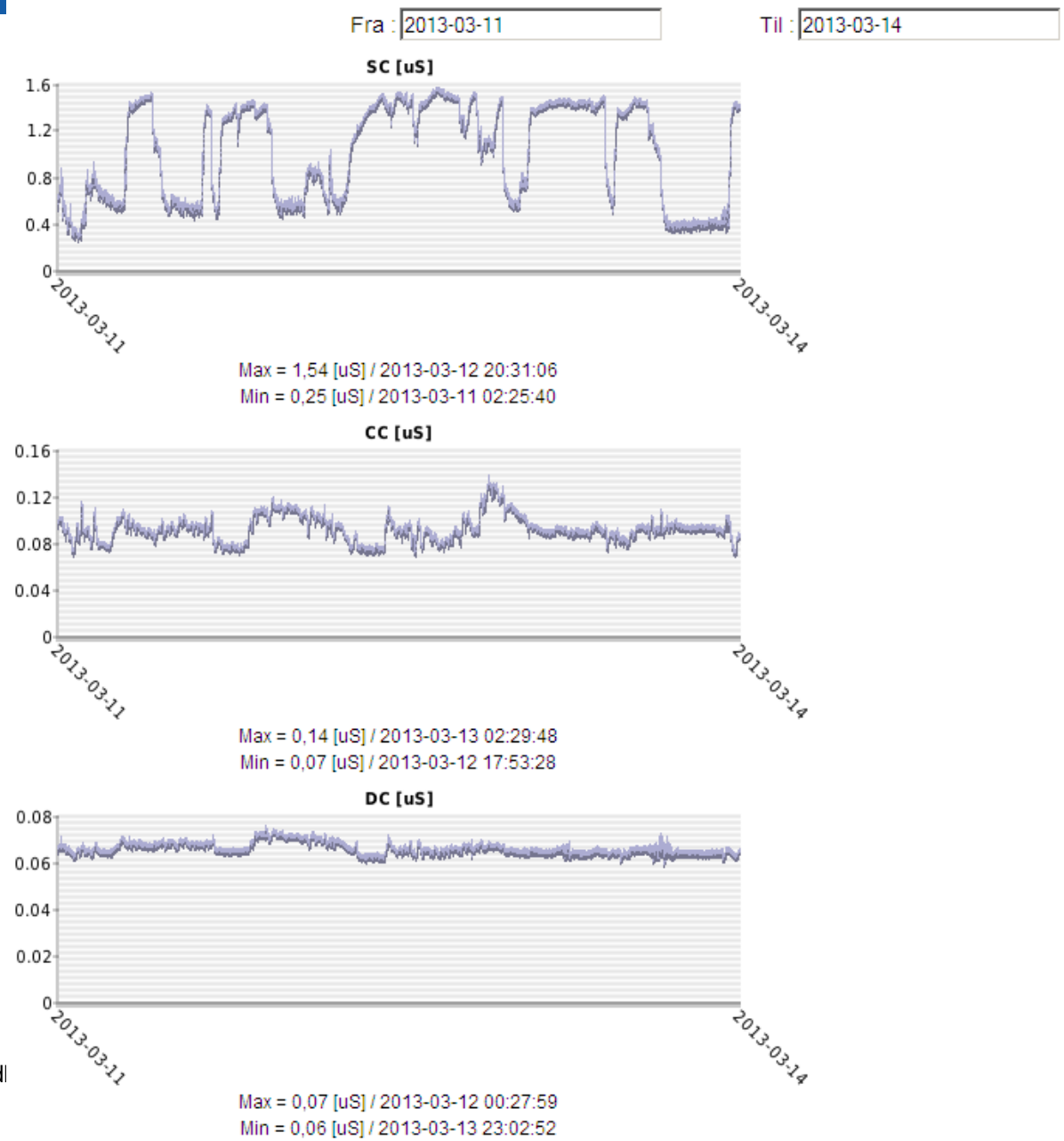
Confidentiality - None (C1)

Data logging via mobile connection and web-page

The analyser is set-up through a web-page at www.fieldit.dk

The measured values are transmitted to the server, e.g every 15 min

Measurement are presented graphically and may be downloaded for further processing



Confidentiality - None (C1)

Degassed conductivity as a tool to dig deeper

Vattenfall CHP – Plant 3

- Biomass fired CHP, drum boíler, medium pressure range
- Conditioning (set-up and control: Ashland)
  - Feedwater: Amersite 1824 (DEHA oxygen scavenger)
  - Boilerwater: Drewphos (sodium phosphate)
- Surveillance & chemistry control
  - SC and pH measured in feedwater, steam and boiler water
  - Dosing of chemicals according to pH of feedwater and boiler water
  - CC not measured at all – only possible by conductivity cells usually used for SC and never tried in practise
- First visit and lab analysis:
  - Conditioning of boilerwater with phosphate OK
  - Conditioning of feedwater:
    - SC, pH and ammonia content matched?
    - CC in both feed water and steam ~ 1 µS/cm
    - High levels of acetate in feedwater and steam, no anions of mineral acids
    - High levels of oxygen in condensate, 20-30 µg/kg in feedwater
    - Very low levels of iron in all samples
- Recommendation initially:
  - Turn to classic conditioning, monitor CC continuously
  - Reduce stress in the turbine condensation zone
  - The management did not listen, amine conditioning continues

Confidentiality - None (C1)

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

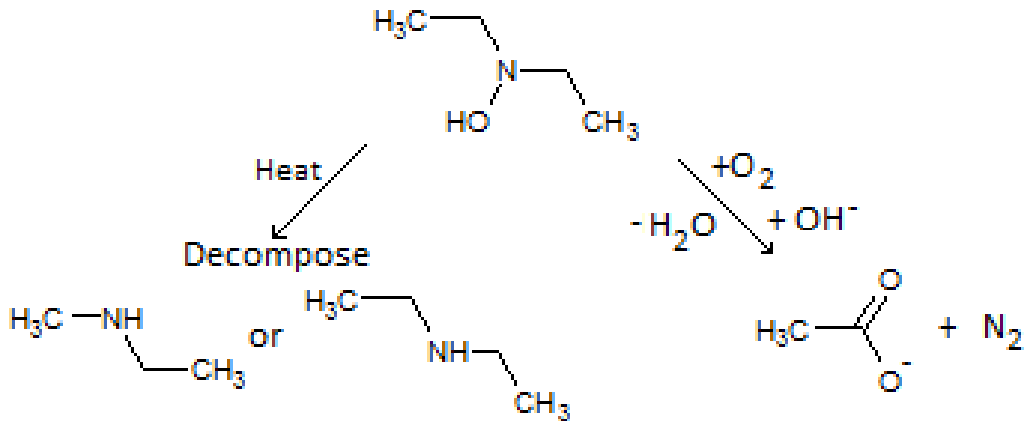
Ref. www.awt.org/certification/quiz4.pdf

Reaction with oxygen:

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

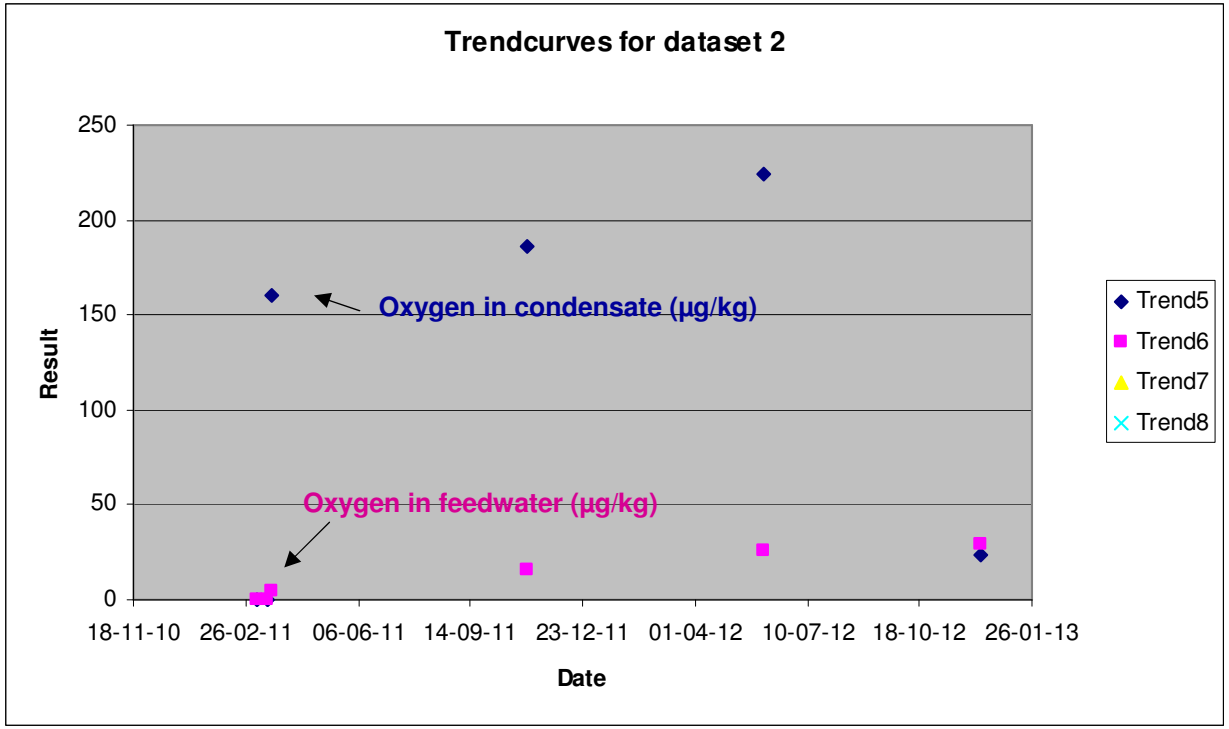
Decomposes when heated to amines:

- diethylamine and methyl-ethyl-amine formed



Confidentiality - None (C1)

Function as oxygen scavenger and for passivation



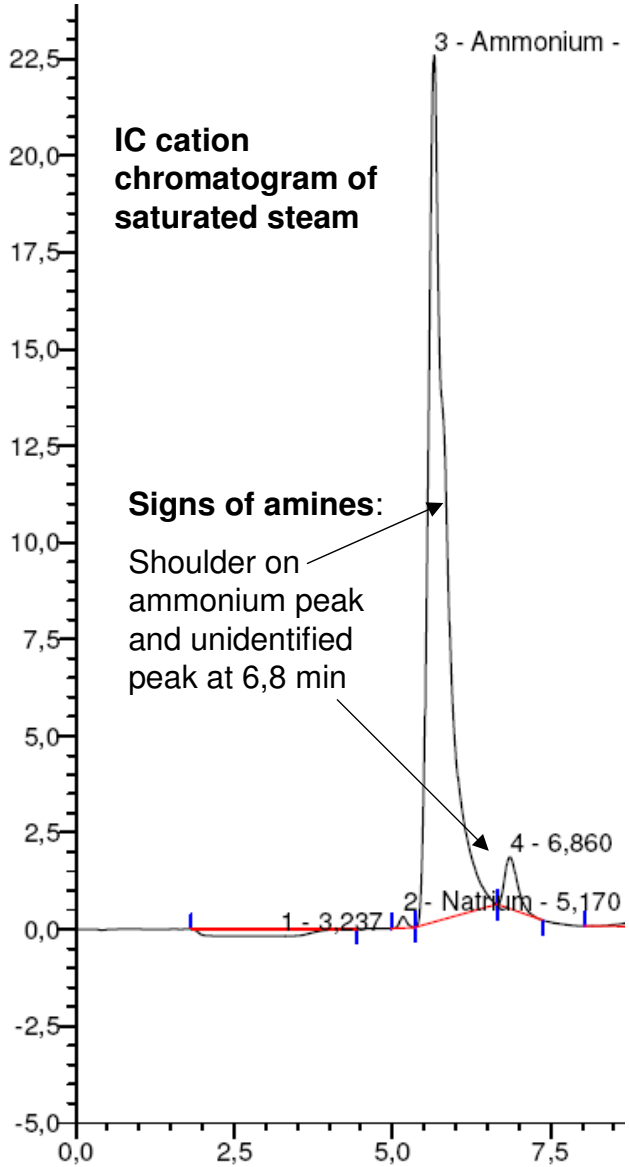
Parameter	Iron, total	Iron, total	Iron, total	Iron, total
Unit	µg/kg	µg/kg	µg/kg	µg/kg
Sample time	Feedwater-Fe	Boilerwater-Fe	SupSteam-Fe	Cond-VK-Fe
08-03-11 00:00	1	1	1	3
21-03-11 14:30	2	3	2	3
04-11-11 11:00	1	3	1	6
31-05-12 10:00	2	3	3	1
Week 39, 2012	41	2	43	137
Week 45, 2012	3	2	1	6
12-12-12 09:00	3	3	1	4

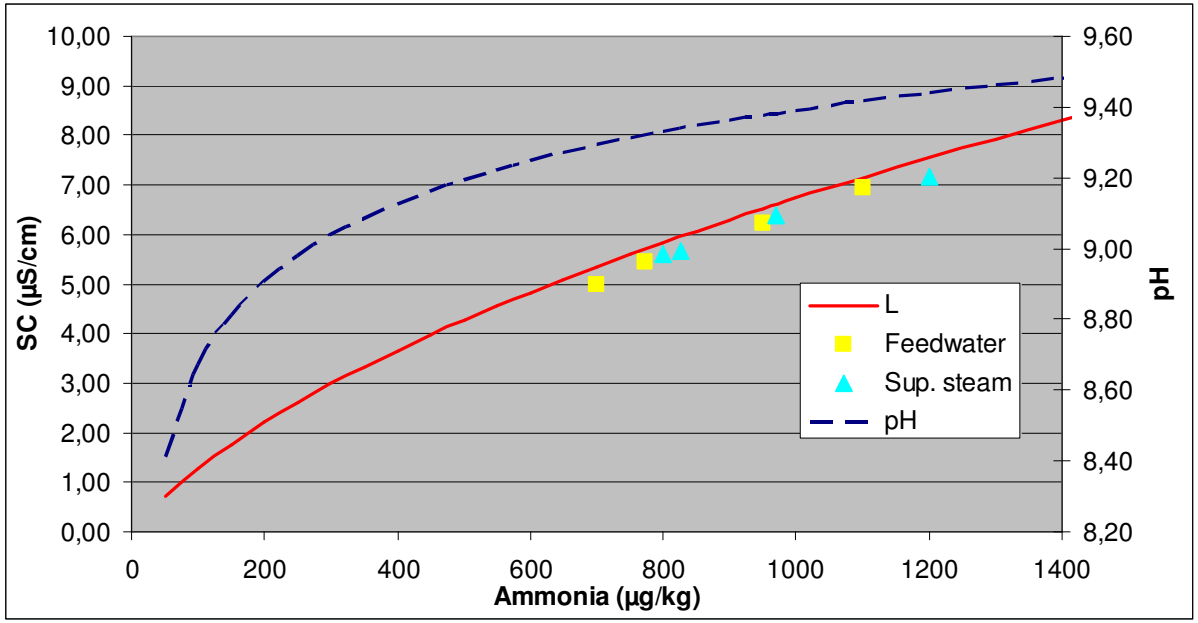
Evaluation:

- Even with high oxygen levels in condensate, the level in feed water is at spec. – could be due to DEHA or efficient deaeration in feedwater tank
- Even with oxygen in the system, very low levels of iron are generally seen. Corrosion protection is OK

Confidentiality - None (C1)

Degradation of DEHA – amines or ammonia?

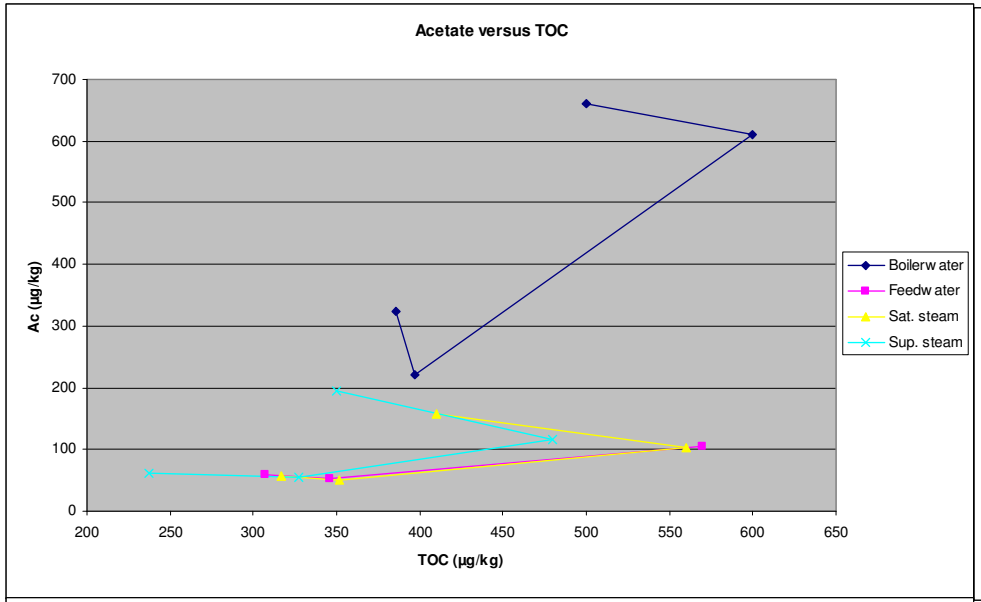


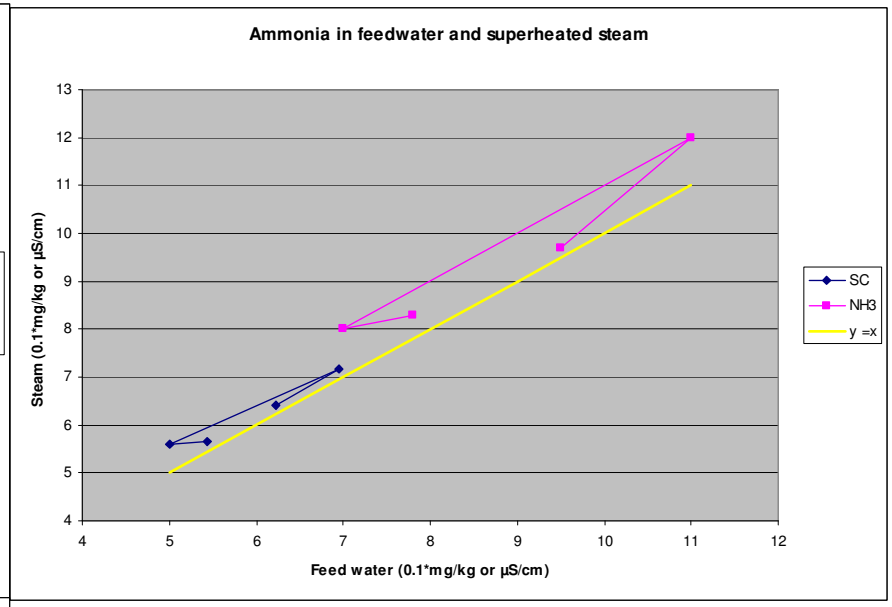


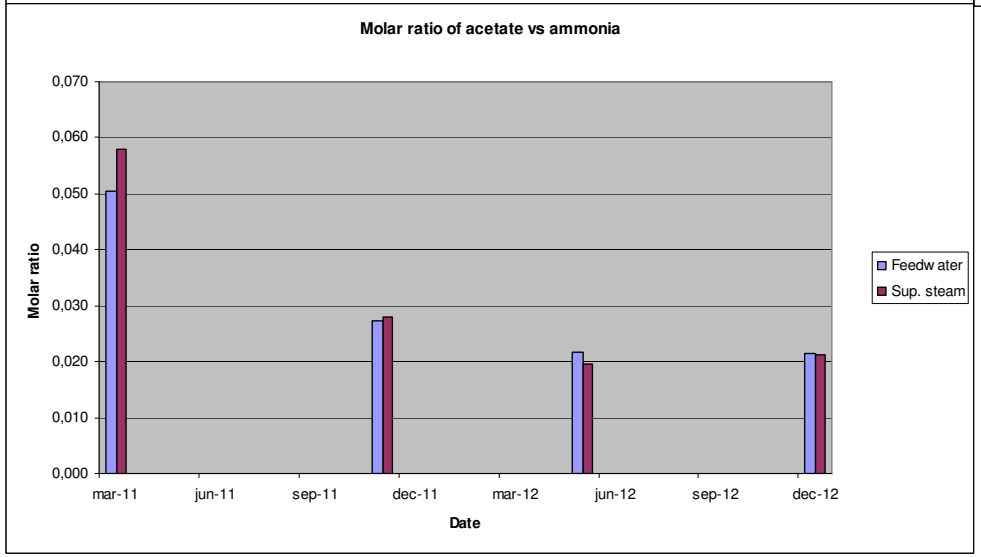
- Ammonia analysed by means of a spectro-photometric method using Nesslers reagent – is perhaps sensitive to amines also?
- Measured ammonia and conductivity matches theory closely
- Cation IC shows signs of both ammonium and amines
- Ammonia may be a major breakdown product!

Confidentiality - None (C1)

Degradation of DEHA – formation of acetate







- Feedwater and steam:
  - TOC in the range 200-600 µg/kg (DEHA & breakdowns)
  - Acetate in the range 50-200 µg/kg
- Boiler water:
  - TOC in the range 350-650 µg/kg
  - Acetate in the range 200-700 µg/kg
- Clear signs of significant degradation by passage of the boiler
- Acetic acid clearly neutralised by ammonia/amines in condensate and feedwater – but what happens in the first condensate zone?

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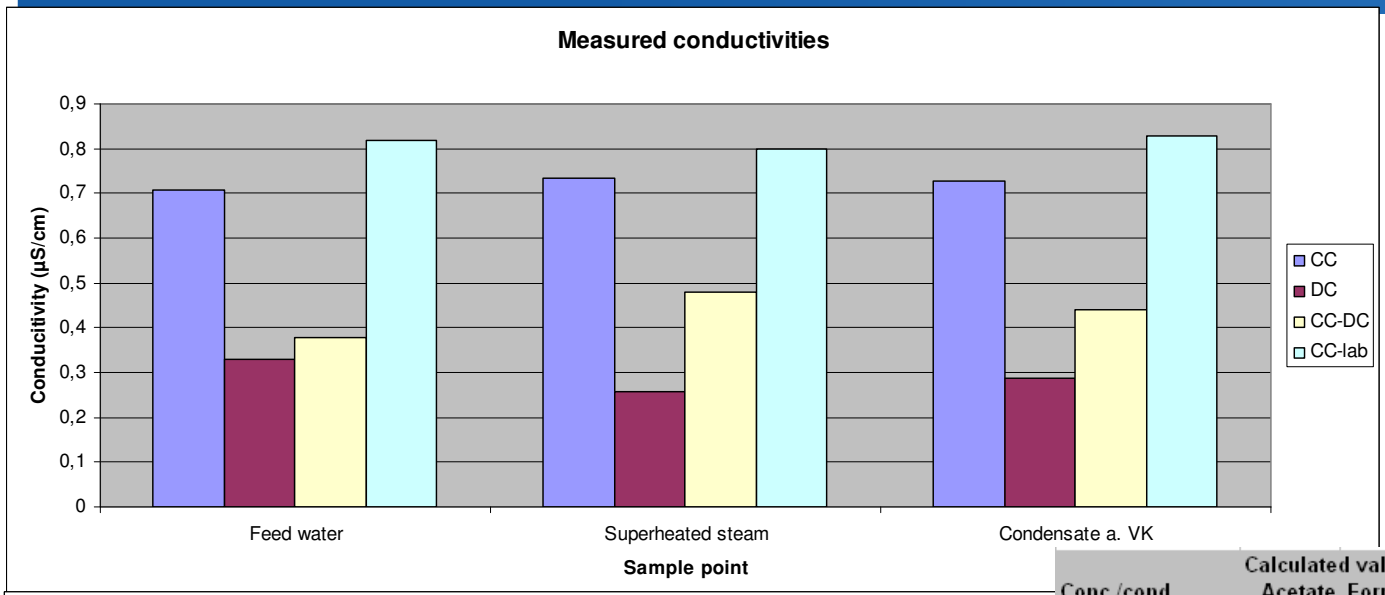
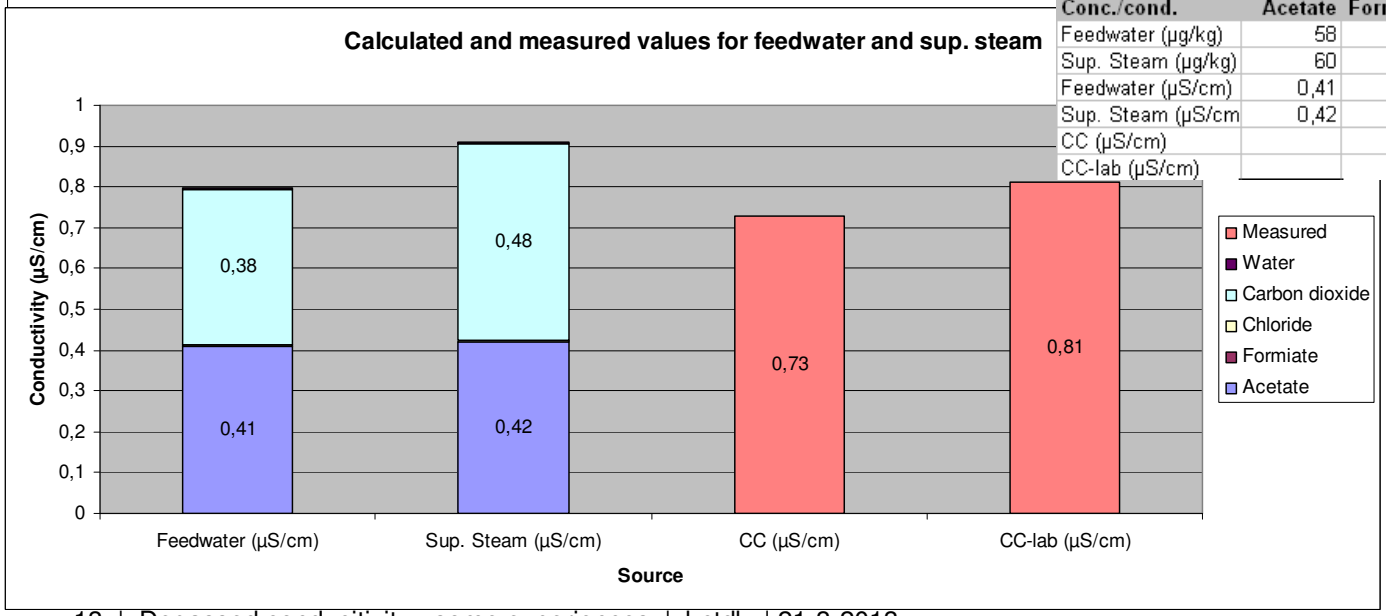
Explanation of the acid conductivity



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

Conc./cond.	Acetate	Formiate	Chloride	Carb.dioxide	Water	Measured
	Calculated values (conc. In µg/kg, conductivity in µS/cm)					
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

- Swan Deltacon analyser
  - After the initial lessons learned about the ion exchanger and the flow rate for high purity samples, the analyser works very well
  - The results compares very well with on-line and lab measurements
  - The analyser is bulky and heavy but may be used as portable with help from the operating personnel
  - The analyser may operate with only attention once a day, results may be watched by means of the web-interface
  - The web-interface is simple and easy to use – data must be downloaded for further/advanced use

- Experiences with DEHA conditioning
  - Dosing to achieve suitable pH and low levels of oxygen works, even in the case of air in-leakage
  - Corrosion protection seems to work well
  - Alkalisation takes place through amines and most likely ammonia formed as breakdown products
  - The usual relation between ammonia, SC and pH seems to apply -> easy dosing control regarding pH
  - DEHA is recommended as oxygen scavenger for conservation also – may be a good choice
  - The initial question on the stress from acetic acid on the turbine remains - other experiences?

Confidentiality - None (C1)