Poster Number E 322,
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[E 322] - The Cell Temperature of ECC Ozonesondes in Relation to the Measured Pump Temperature: Impact of Freezing and Boiling Effects Observed During JOSIE

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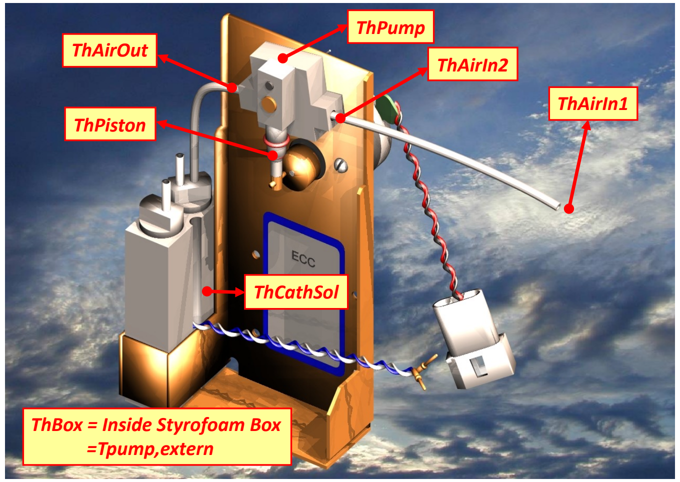
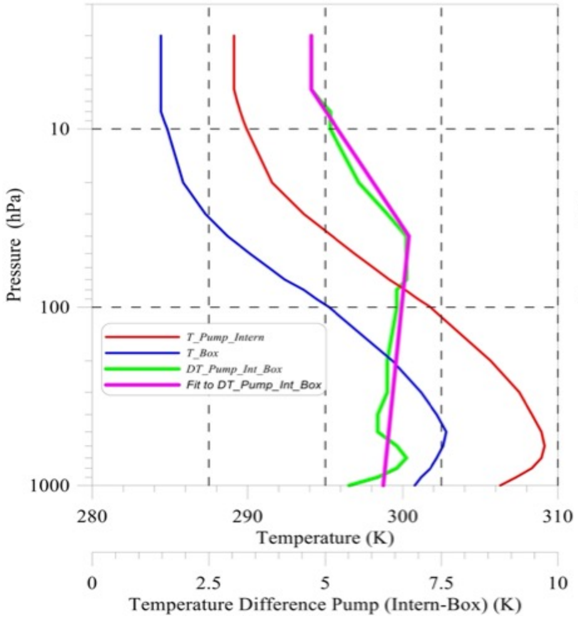
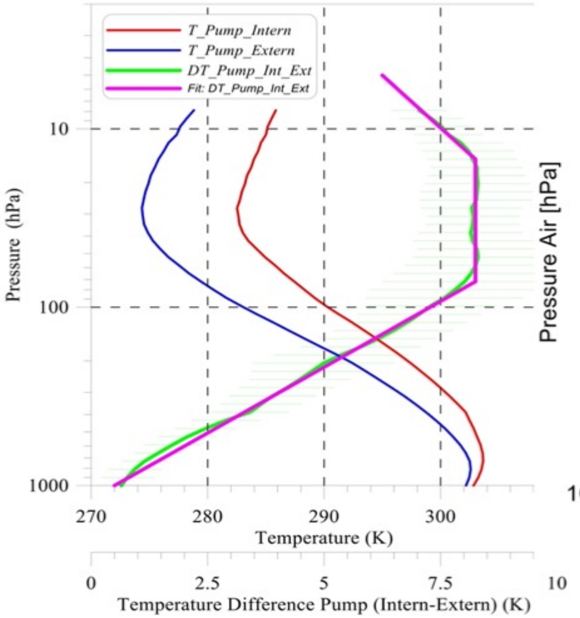
50 Years of ECC Pump Temperature Measurements: The “Truest” Pump Temperature



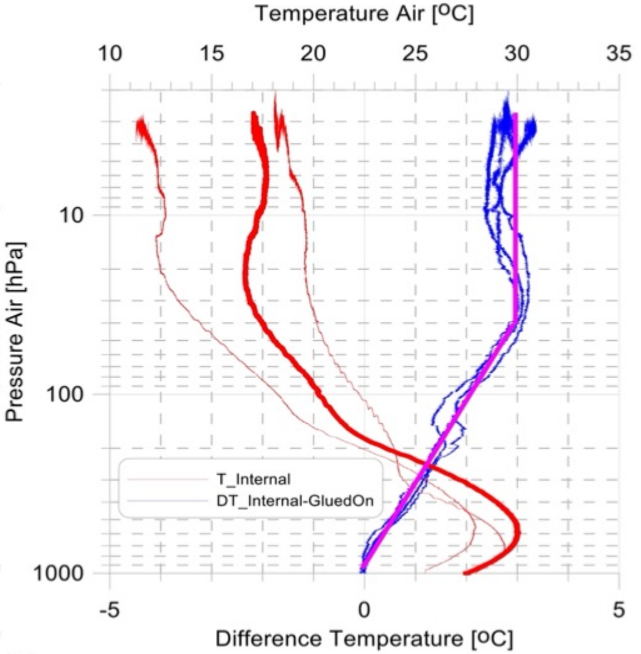
1. For balloon borne electrochemical concentration cell (ECC) ozonesondes an accurate measurement of the pump temperature is essential for accurate ozone measurements.
2. During more than 50 years of ozonesoundings the locations of the pump temperature sensor have changed several times, which caused significant inhomogeneities in the long term ozonesonde records.
3. In simulation chamber experiments conducted at the World Calibration Center for Ozone Sondes (WCCOS), these pump temperature inhomogeneities have been characterized and corresponding correction functions were derived.
4. The corrections were successfully applied in O3S-DQA (Ozone Sonde Data Quality Assessment) such that nowadays the best representative (“truest”) pump temperature can be determined within an uncertainty better than 0.7 K [1][2].



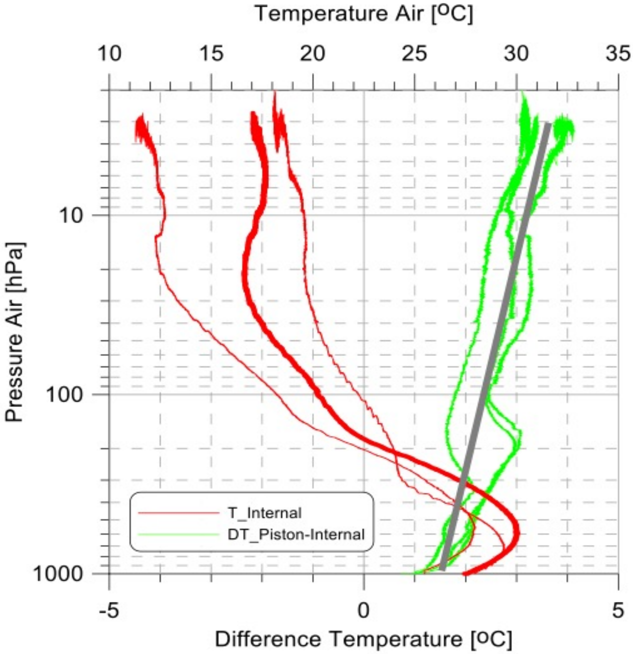
Case 1: Box Temperature (< 1990)
(Thermal Rod: SPC-1A/2A/3A/4A)



Case 2 &3 : Box Temperature (1990-1996)
(Thermister in box or taped at Pump:: SPC-5A

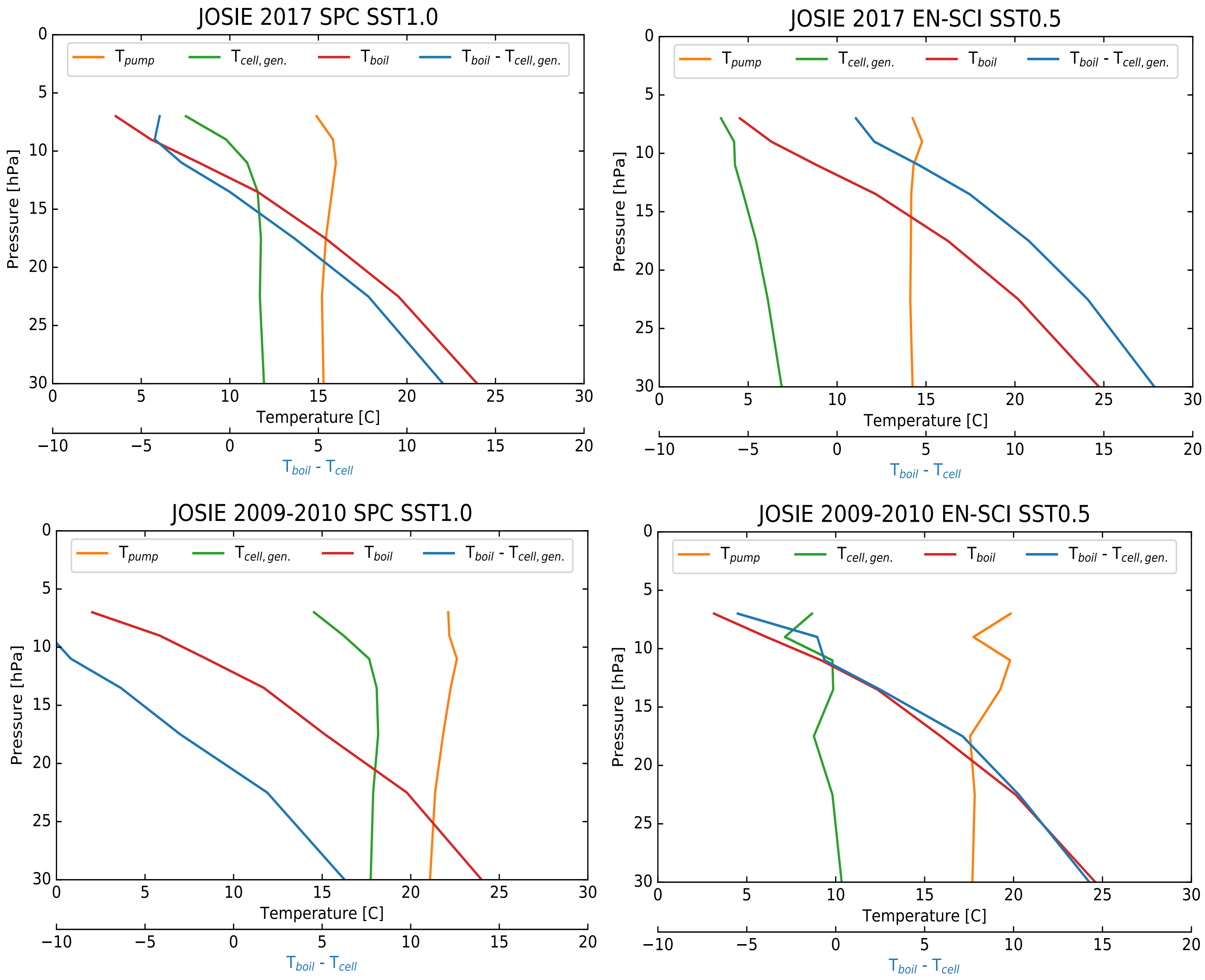


Case 4 : Internal Temperature (>1996)
(Thermister in Pump Base: SPC-6A & ENSCI)



“Truest” Pump. Temperature
(Internal to Piston: SPC & ENSCI)

Relation Cathode Cell and Pump Temperature: Potential of Freezing and Boiling of Sensing Solution



- In 2017 during JOSIE-SHADOZ [3] the internal pump and cathode cell temperature were measured simultaneously (see upper graphs).
- Significant differences $T_{P,Int}$ and T_{Cell} were observed, which were largest for the ENSCIs.
- The air pressure dependent characteristic of the observed differences have been applied to calculate a generic cell temperature for the JOSIE 2009/2010 data compared to SPC-sondes (see lower graphs).
- During JOSIE 2009/2010 the pump and cell temperatures were about 5 to 10 degrees Celsius larger than in JOSIE 2017
- A proper cell temperature is important such that no freezing or low boiling effects of the sensing solutions can occur in the course of a sounding.
- Freezing or boiling effects will have a negative impact on the ozonesonde performance, most likely in the upper part of the sounding, above 20-25 km altitude.

Cathode Cell Temperature and Boiling Pressure: Potential of Vigorous Evaporation of Sensing Solution (1)

- In all JOSIE experiments the "flown" ECC-cells have been weighted before and after the "sounding".
- The difference in weight, i.e. weight loss, is a direct measure of the amount of cathode sensing solution that has been lost through evaporation of spraying out of the cathode cell.
- The spraying of the cells have been observed in the laboratory by running an ECC sonde in a glass tank at low pressures, until 5 hPa or even lower.

JOSIE 2000

Parameter	Sensing Solution Type 1% KI, Full Buffer		Sensing Solution Type 0.5% KI, Half Buffer	
Sonde Type	SPC-6A	ENSCI	SPC-6A	ENSCI
Delta Mass Sensing Solution [g]	0.71±0.42 *(N=7)*	0.67±0.34 *(N=7)*	1.75±0.66 *(N=5)*	0.67±0.12 *(N=8)*

JOSIE 2009/2010/2017

2009-2010 Solution loss [gr]	EN 0.5%-0.%B (16)	EN 1.0%-1.0B (25)	SP 0.5%-0.5B (19)	SP 1.0%-1.0B (23)
Difference in sonde weight	1.03 ± 0.38	1.15 ± 0.26	2.45 ± 0.67	2.44 ± 0.59
2017 Solution loss [gr]	**EN 0.5%-0.%B** (20)	**EN 1.0%-0.1B** (25)	**SP 1.0%-0.1B** (9)	**SP 1.0%-1.0B** (14)
Difference in sonde weight	0.52 ± 0.04	0.49 ± 0.07	0.87 ± 0.17	0.92 ± 0.22

- Losses of sensing solution are for SPC sondes about a factor two larger than ENSCI sondes when flowing at similar pump, ie. cell temperatures.
- The cell temperature determines the saturation vapour pressure of liquid water (i.e. sensing solution).
- The sensing solution starts to boil as soon the saturation vapour pressure of liquid water of the sensing solution exceeds the ambient air pressure.
- The boiling induces a strong and vigorous bubbling (i.e. spraying) and evaporation of the sensing solution.
- The vigorous evaporation and spraying can lead to substantial losses of sensing solution, as occurred in JOSIE 2009/2010.

Cathode Cell Temperature and Boiling Pressure: Potential of Vigorous Evaporation of Sensing Solution (2)

The two round molded plastic half-cells of the sensing cell are just mounted with two screws at the metal frame structure of the sonde body:
Limited thermal contact.

The rectangular two half cells of the sensing cell are integrated (i.e. embedded) in the metal frame structure of the sonde:
Good thermal contact.

- Compared to JOSIE 2000 and 2017 the sondes at JOSIE 2009-2010 were operated at higher (5-10 ^{o}C larger) pump (i.e. cell) temperatures and the cell starts to boil already at higher ambient air pressures.
- Loss of more sensing solution due to boiling and strong evaporation effect at pressures lower than 10-15 hPa.
- The effect is most pronounced for the SPC sondes, due to the way the sensing cell is integrated (i.e. embedded) in the metal frame structure of the SPC sonde, which causes a good thermal contact and thus efficient heat exchange between the metal frame and the Teflon cell.
- This in contrast to the ENSCI sonde where the sensing cell, consisting of two round molded plastic tubes, is only mounted with two screws at the metal frame (with very little thermal contact with the metal frame), such that the heat exchange between metal frame and sensing cell is much less efficient as for the SPC sonde.
- This means that for the SPC the more efficient heat exchange can cause a much more efficient evaporation as soon as the boiling point has been reached, i.e. exceeded.

Fraction of Losses of Sensing Solution of SPC6A and ENSCI-Z Sondes Due to Evaporation and Spraying

Fraction of the weight losses of sensing solution due to evaporation and spraying,respectively, were obtained by weighting and Iodide-determination (with Iodid specific ionometer) of the sensing solution before and after 10-30 min. of operation at constant, but low air pressures (5-30 hPa)

Fraction of Evaporation and Spraying related to weight lossess

Pressure Air [hPa]	Evaporation (fraction in %)		Spray (fraction in%)	
	SPC6A	ENSCI	SPC6A	ENSCI
30	100	100	0	0
20	86	86	14	14
10	76	97	24	3
5	80	78	20	22
5 (with pre-cooling)	80	98	20	2
2 (with pre-cooling)	79	94	21	6

- Besides the stronger evaporation (boiling), the SPC sondes also tend to a stronger spraying effect.
- Evaporation will cause losses of sensing solution but also increase the KI (i.e. buffer) concentration, which can cause an increase of stoichiometry (i.e. sensitivity of the ECC).
- Too large losses of sensing solution will finally cause a decrease of the ozone absorption efficiency into the sensing solution.

Steady State Experiment: T_{Sol} and $P_{Sat,H2O}(T_{Sol})$ at Different P_{Air}

Pressure Air [hPa]	Temperature Solution [^{o}C]		Saturation Pressure H2O [hPa]	
	SPC6A	ENSCI	SPC6A	ENSCI
30	23	22.5	28.1	27.2
20	18	18	20.6	20.6
10	8.5	8.5	11.0	11.0
5 (with pre-cooling)	2	1.5	7.0	6.7
2 (with pre-cooling)	-1	0-4	5.7	6.1-8

- Evaporation tends to decline the solution temperature (T_{Sol})
- In case of passive or active electrical heating the heat energy will be primarily deployed to increase T_{sol} as long $P_{Sat,H2O}(T_{Sol}) < P_{Air}$
- As soon as $P_{Sat,H2O}(T_{Sol}) = P_{Air}$ is achieved the solution will start to boil and an enhanced evaporation i.e.cooling will occur whereby even at larger amounts of heating T_{Sol} will adjust in order to keep $P_{Sat,H2O}(T_{Sol}) = P_{air}$ Cautious here: More heating-> More Evaporation > More losses of sensing solution

What is the Optimal Pump Temperature? Avoid Freezing BUT also Boiling (Strong Evaporation)

1. The losses of sensing solution for SPC6A are larger than for ENSCI.
2. This is most likely caused to the different ways the electrochemical cell are mounted at the metal frame of the ECC-sonde, whereby the thermal contact of SPC6A-cell to the metal frame is more efficient than for the ENSCI-cell.
3. In the course of the sounding the cell temperatures are generally getting lower than the pump temperatures: SPC-6A sondes (0-5 ^{o}C) and ENSCI sondes (0-10 ^{o}C).
4. Optimum pump temperature should be as low as possible to prevent strong losses of sensing solution due to evaporation or spraying at reduced pressures, particularly when the potential of boiling has achieved.
5. On the other hand, to avoid freezing, the SPC pump temperature should not be lower than +5 ^{o}C and the ENSCI pump temperature not lower than +10 ^{o}C.
6. The more the saturation water pressure (P_{satH2O}) is exceeding the air pressure (P_{Air}) the more (stronger) the evaporation due to boiling of the sensing solution will occur. This will decline the solution temperature (T_{Sol}) whereby the system tends to achieve still equilibrium and thus P_{SatH2O} (T_{Sol}) tends to approach P_{air}.
7. This means that, when electrical heaters are used to avoid any freezing of the sensing solution, these should only be active when the pump temperature falls below a certain threshold.

References

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[2] Smit, H.G.J., et al., Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Jülich Ozone Sonde Intercomparison Experiment (JOSIE), *J. Geophys. Res.,* 112, D19306, doi:10.1029/2006JD007308 (2007).

[3] Thompson, A. M., et al., Ozonesonde Quality Assurance: The JOSIE-SHADOZ (2017) Experience, *Bull. Am. Meteor. Society*, *100(1)*, doi.org/10.1175/BAMS-17-0311 (2019).