MEM7 – Application Note Temperature Compensation

Content

1. General

The output signal of an electrochemical sensor varies with temperature.

This is mostly due to the temperature dependence of the sensitivity, which generally increases with increasing temperature and is at -40°C much lower than at room temperature. However, depending on the sensor type there can be a shift in baseline as well which again affects the output signal. The latter is primarily at high temperatures and most notable with biased sensors.

Basically, the temperature dependence of a sensor is given by the nature of the gas, the nature of the specific components inside the sensor and their chemical reaction within.

2. Temperature dependence curves

It is highly recommended to acquire the temperature dependence curves with the entire instrument. The sampling system, the humidity, the electronics, the interaction between the electronics and the sensor, all have a significant impact on the temperature dependence of the final measurement reading.

In some of Membrapor’s sensor data sheets you will find sensor specific temperature dependence curves of the baseline and/or the sensitivity. This data is acquired at our factory, using the in-house sampling system and raw analogue signal.

3. Collecting data for the temperature dependence

Be aware of abrupt humidity changes during cooling and heating cycles and keep the relative humidity between 15-90 %, i.e. inside the range specified for electrochemical sensors. Condensation onto the sensors must be avoided as it can falsify the results.

3.1. Procedure for the temperature compensation of the output signal (TCS)

3.1. Place one or more instruments with the Membrapor sensors installed in a temperature (or climate) chamber.

3.2. Start at a high temperature (e.g. 50°C) and wait for 2 hours until the instrument and all components have warmed up. Take the baseline signal.

3.3. Expose the sensors to a common target gas concentration in the intended application and collect the signals when they are stable.

3.4. Cool down in steps convenient for you, e.g. in steps of 10°C. At each step, wait for the instrument and components to adapt to the new temperature (up to 1 hour). Take the baseline signal. Then expose the sensors to the same target gas concentration as above and collect the signals.

3.5. Be careful around the freezing point of water when cooling down from +10°C to -10°C, especially in cases with high humidity. Avoid condensation onto the sensors.

The result will be XY data with the signal output of the sensors (Y) at certain temperatures (X). This data is used to calculate the temperature compensation function TCS, see chapter 4 (formula) and chapter 5.2 (example).

3.2. Procedure for the temperature compensation of the baseline (TCZ)

Use the same procedure explained above but do not apply any target or interference gas (only the background gas related to the application). Instead collect the baseline signals at each step. Use the generated data to calculate the temperature compensation function TCZ, see chapter 4 (formula) and chapter 5.1 (example).

4. Formula

This chapter explains how to calculate the ppm value of a sensor signal applying temperature compensation functions.

4.1. Temperature compensation functions TCx

The temperature compensation is at reference temperature. For the baseline, this temperature is called T_{BL} and for the sensitivity T_{cal}, as calibration for the baseline and the sensitivity may be done at different temperatures.

$TCS(T, T_{cal})$	is the temperature compensation of the sensitivity of the sensor.
$TCZ(T, T_{BL})$	is the temperature compensation of the baseline of the sensor.
$TCG(T, T_{cal})$	is the temperature compensation of the gain factor (only in 4-electrode sensors)

Commonly a polynomial of 3rd degree with the following form is used to account for the temperature dependence of an electrochemical sensor:

$$Fit(T) = k_0 + k_1 T + k_2 T^2 + k_3 T^3$$

The coefficients k_0, k_1, k_2 and k_3 are gained from data acquired in the temperature measurement (see chapter 3 and chapter 5). For the four coefficients at least four measurement points are needed to define them mathematically correct.

To achieve the correct baseline shift (usually 0 ppm) and reference sensitivity (usually 100%), the polynomial must be adjusted to the calibration temperatures. For TCZ, the obtained fit is evaluated at T_{BL} and this value is subtracted from the fit polynomial to give TCZ. This is equivalent to adjusting the coefficient k_0 as desired:

$$TCZ(T, T_{BL}) = Fit(T) - Fit(T_{BL})$$

For TCS and TCG the polynomial is adjusted to match the calibration value at the calibration temperature T_{cal} by renormalizing:

$$TCS(T, T_{cal}) = Fit(T)/Fit(T_{cal})$$

$$TCG(T, T_{cal}) = Fit(T)/Fit(T_{cal})$$

For a detailed procedure see chapter 5.

4.2. ppm value formula

For 3-electrode sensors, the following formula can be used to calculate the ppm-value of a target gas:

$$ppm = \left(\frac{I_s - I_{s,0}}{a}\right) \cdot TCS(T, T_{cal}) + TCZ(T, T_{BL})$$

If used with 4-electrode sensors, the formula has an additional term due to the auxiliary electrode:

$$ppm = \left(\frac{I_s - I_{s,0} - G \cdot \left|I_a - I_{a,0}\right| \cdot TCG(T, T_{cal})}{S}\right) \cdot TCS(T, T_{cal}) + TCZ(T, T_{BL})$$

where

I_s	current at the sensing electrode during the measurement (in nA)
I_a	current at the auxiliary electrode during the measurement (in nA)
$I_{s,0}$	baseline current at the sensing electrode (in nA)
$I_{a,0}$	baseline current at the auxiliary electrode (in nA)
a	sensitivity of the sensing electrode (determined during calibration)
G	gain factor of the auxiliary electrode (determined during calibration)
S	sensitivity of a 4-electrode sensor (in nA/ppm, determined during calibration)

A detailed procedure for the calibration of a 4-electrode sensor and the calculation of the *G* and the *S* can be found in application note MEM6.

5. Example

Let us assume the following temperature dependence measurement where the CO sensitivity is characterized:

- Temperature range: between -20 and +60°C. (9 measurement points)
- CO concentration: 701.5 ppm (H2 concentration: 0 ppm)
- Sensor: 16 example CO sensors (4-electrode, range 0-2000 ppm)
  average sensitivity: 67 nA/ppm, average gain: 1.43
- Calibration of both sensitivity and baseline done at 20°C
- Measurement: see Figure 1, data acquired: see Table 1

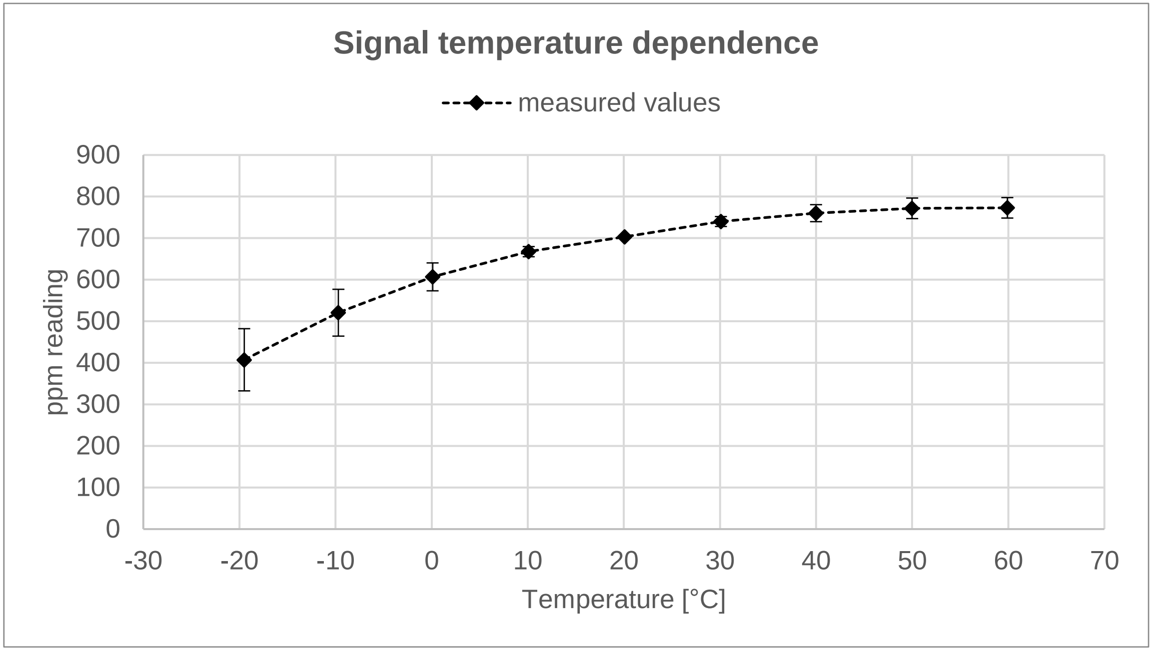

Figure 1: Median value of the output signals of example sensors in dependence of the temperature. Error bars representing the standard deviation.

Table 1: Acquired data from temperature measurement. Baseline and output signals are median values.

Example sensor median values

Temp. [°C]	Gas conc. [ppm]	Output signal ppm reading	Baseline ppm reading
-20	701.5	407.4	1.0
-10	701.5	520.6	0.6
0	701.5	606.8	0.7
10	701.5	667.5	0.6
20	701.5	703.4	1.8
30	701.5	740.0	2.6
40	701.5	760.0	3.8
50	701.5	771.7	7.8
60	701.5	772.9	13.9

5.1. Calculating the coefficients of TCZ(T,T_{BL})

For the TCZ compensation function, only the baseline signal is needed. A referenced baseline can be calculated by subtracting the baseline at the reference temperature (20°C) from each baseline signal. Its negative values are called the corresponding compensation factors, see Table 2:

Table 2: Referenced baseline signal (relative to 20°C) and compensation factors.

Referenced baseline and compensation factors				
Temp.	Gas conc.	Baseline	Referenced baseline	Compensation factors
[°C]	[ppm]	ppm reading	ppm reading	ppm reading
-20	701.5	1.0	-0.8	0.8
-10	701.5	0.6	-1.2	1.2
0	701.5	0.7	-1.1	1.1
10	701.5	0.6	-1.2	1.2
20	701.5	1.8	0.0	0.0
30	701.5	2.6	0.8	-0.8
40	701.5	3.8	2.1	-2.1
50	701.5	7.8	6.1	-6.1
60	701.5	13.9	12.2	-12.2

The set of compensation factors is approximated by a polynomial of 3rd degree, see chapter 4.1:

$$Fit(T) = k_0 + k_1 T + k_2 T^2 + k_3 T^3$$

Each compensation factor gives one equation. So, to determine the four unknown coefficients k_0, k_1, k_2 and k_3 at least four compensation factors are needed. Using calculating application such as Microsoft Excel the coefficients can easily be obtained (see Table 3).

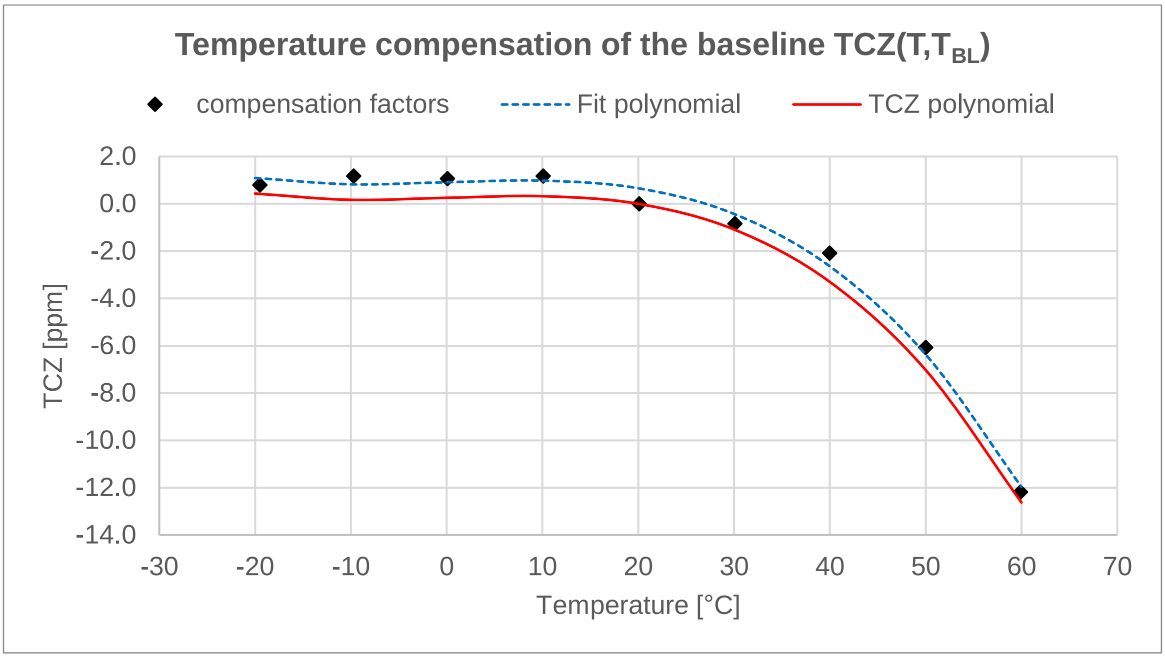

Figure 2: Adjusted and non-adjusted baseline temperature compensation polynomials compared to the measured compensation factors.

However, as can be seen in Figure 2, the determined fitting curve gives a finite value of the baseline at the calibration temperature T_{BL} of 20°C. To adjust this, the obtained fit is evaluated at T_{BL} and this value is subtracted from the fit polynomial to give TCZ. This is equivalent to adjusting the coefficient k_0 as desired:

$$TCZ(T, T_{BL}) = Fit(T) - Fit(T_{BL})$$

The TCZ(T,T_{BL}) together with the determined coefficients k_0, k_1, k_2 and k_3 can then be used to calculate the baseline ppm-value according to chapter 0.

Table 3: Coefficients k_0, k_1, k_2 and k_3

Fit coefficients				
	k3	k2	k1	k0
	[-]	[-]	[-]	[-]
fitted	-6.2E-05	-9.2E-05	1.4E-02	***9.1E-01***

evaluation of the fit at T_{BL}			T_{BL}	Fit(T_{BL})
			[°C]	[-]
			20	6.6E-01
TCZ coefficients				
	k3	k2	k1	k0
	[-]	[-]	[-]	[-]
adjusted	-6.2E-05	-9.2E-05	1.4E-02	***2.5E-01***

5.2. Calculating the coefficients of TCS(T,T$_{cal}$)

For the calculation of the sensitivity temperature compensation function TCS(T,T$_{cal}$), first the baseline signal is subtracted from the sensor output signal (Table 4):

Table 4: Sensitivity signal obtained by subtracting the baseline from the sensor output.

Sensor signals				
Temp. [°C]	Gas conc. [ppm]	Output signal ppm reading	Baseline signal ppm reading	Sensitivity signal ppm reading
-20	701.5	407.4	1.0	406.4
-10	701.5	520.6	0.6	520.0
0	701.5	606.8	0.7	606.1
10	701.5	667.5	0.6	666.9
20	701.5	703.4	1.8	701.6
30	701.5	740.0	2.6	737.4
40	701.5	760.0	3.8	756.2
50	701.5	771.7	7.8	763.9
60	701.5	772.9	13.9	759.0

A normalized sensitivity signal relative to the signal at 20°C can be calculated at each temperature. The inverse values are the corresponding compensation factors, see Table 5:

Table 5: Normalized sensitivity and compensation factors (relative to 20°C)

Normalized sensitivity and compensation factors					
Temp.	Sensitivity signal	Normalized sensitivity		Compensation factors	
[°C]	ppm reading	[-]	[%]	[-]	[%]
-20	406.4	0.58	58%	1.73	173%
-10	520.0	0.74	74%	1.35	135%
0	606.1	0.86	86%	1.16	116%
10	666.9	0.95	95%	1.05	105%
20	701.6	1.00	100%	1.00	100%
30	737.4	1.05	105%	0.95	95%
40	756.2	1.08	108%	0.93	93%
50	763.9	1.09	109%	0.92	92%
60	759.0	1.08	108%	0.92	92%

The coefficients of the 3rd degree compensation polynomial (chapter 4.1) $Fit(T)$ can again be obtained from the compensation factors by a calculating application such as Microsoft Excel.

Also here, the polynomial needs to be adjusted to match the calibration value at the calibration temperature T_{cal}. This is done by renormalizing, see also Table 6:

$$TCS(T, T_{cal}) = Fit(T)/Fit(T_{cal})$$

Table 6: Coefficients k_0, k_1, k_2 and k_3, before and after renormalization.

Fit coefficients				
	k3	k2	k1	k0
	[-]	[-]	[-]	[-]
fitted	***-3.8E-06***	***4.4E-04***	***-1.7E-02***	***1.2E+00***

		T_{cal}	$Fit(T_{cal})$
evaluation of the fit at T_{cal}		[°C]	[-]
		20	9.7E-01

TCS coefficients				
	k3	k2	k1	k0
	[-]	[-]	[-]	[-]
renormalized	***-3.9E-06***	***4.6E-04***	***-1.8E-02***	***1.2E+00***

Finally, the adjusted $TCS(T, T_{cal})$ and the $TCZ(T, T_{BL})$, together with their respective coefficients k_0, k_1, k_2 and k_3, can be used to calculate the ppm-value of the sensitivity signal and the baseline according to chapter 4.2. See Figure 3 and Figure 2.

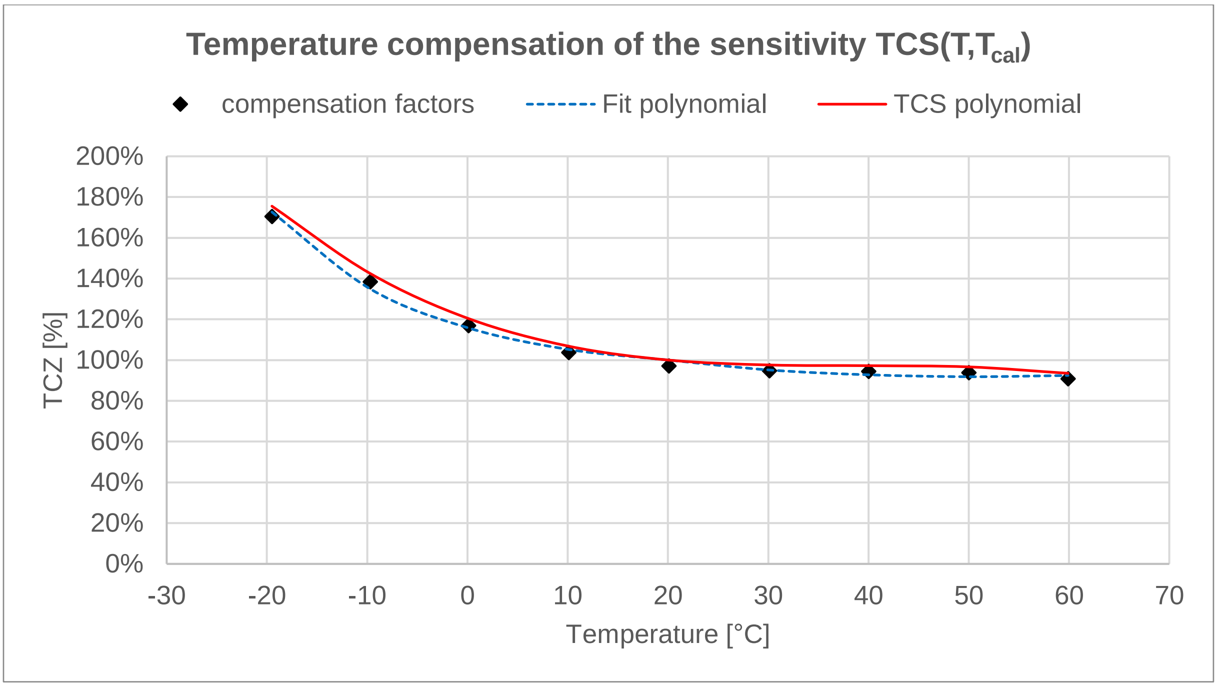

Figure 3: Temperature compensation of the sensitivity TCS. Comparison of measured and calculated and adjusted values, respectively.

5.3. Example of a subsequent recalibration

If the shift of the baseline or the sensitivity is recalibrated at a different temperature, also the temperature polynomials have to be recalculated as they depend on the calibration temperature.

For example, a recalibration of the baseline at 30°C is done. Therefore, the TCZ(T,T_{BL}) should equal zero at this temperature. This can be achieved by directly evaluating the old TCZ at the new T_{BL} and subtracting this value from the old TCZ function (thereby adjusting k_0):

$$TCZ(T,T_{BL}^{new}) = TCZ\left(T,T_{BL}^{old}\right) - TCZ\left(T_{BL}^{new},T_{BL}^{old}\right)$$

The table below shows how the TCZ are affected by the adjustment to the new calibration temperature according to the equation above:

Comparison between old and recalibrated new TCZ		
	old TCZ	new TCZ
Temperature	TBL = 20°C	TBL = 30°C
[°C]	ppm reading	ppm reading
-20	0.4	1.5
-10	0.2	1.3
0	0.3	1.3
10	0.3	1.4
20	0.0	1.1
30	-1.1	0.0
40	-3.3	-2.2
50	-7.0	-5.9
60	-12.6	-11.5

Of course, this would also affect the coefficient of the polynomials (see below), but calculating this is unnecessary.

Old coefficients TCZ			
k3 [-]	k2 [-]	k1 [-]	k0 [-]
-6.2E-05	-9.2E-05	1.4E-02	***2.5E-01***

	T_{BL} [°C]	TCZ(T_{BL}) [ppm]
old TCZ evaluated at new T_{BL}:	30	-1.1E+00

New coefficients TCZ			
k3 [-]	k2 [-]	k1 [-]	k0 [-]
-6.2E-05	-9.2E-05	1.4E-02	***1.3E+00***

Similarly, a recalibration of the sensitivity is performed at 30°. The TCS polynomial should equal 100% at this temperature, which can be ensured by renormalization of the old TCS function. The old TCS function is evaluated at the new calibration temperature and then renormalized to this value, giving the new TCS function.

$$TCS(T, T_{cal}^{new}) = TCS(T, T_{cal}^{old}) / TCS(T_{cal}^{new}, T_{cal}^{old})$$

Please see the table below for an example of how the TCS values are adjusted:

Comparison between old and recalibrated new TCS

	old TCS	new TCS
Temperature	Tcal = 20°C	Tcal = 30°C
[°C]	[%]	[%]
-20	177%	182%
-10	143%	147%
0	121%	124%
10	107%	110%
20	100%	102%
30	98%	100%
40	97%	100%
50	97%	99%
60	93%	96%

Identically to the example for TCZ, the coefficients are affected by the shift, however calculating them is once again unnecessary:

Old coefficients TCS

k3 [-]	k2 [-]	k1 [-]	k0 [-]
-3.9E-06	***4.6E-04***	***-1.8E-02***	***1.2E+00***

	T_{cal} [°C]	TCS(T_{cal}) [-]
old TCS evaluated at new T_{cal}:	30	9.8E-01

New coefficients TCS

k3 [-]	k2 [-]	k1 [-]	k0 [-]
-4.0E-06	***4.7E-04***	***-1.8E-02***	***1.2E+00***