MEM9 – Application Note VOC Sensor

1. Sensor principle

A detailed description of the sensor's operation principle can be found in application note MEM1. In the following only a short description is provided. MEMBRAPOR's amperometric gas sensors provide an electric current which is directly proportional to the gas concentration. This current is generated, when the target gas diffuses through the capillary and is either oxidized or reduced on the sensing electrode. With a potentiostatic circuit the sensing electrode maintains a fixed potential with respect to the reference electrode. Finally, the counter electrode balances out the net electrons. The ionic current between sensing and counter electrode is transported by the dissociated electrolyte in the sensor body. An in-depth physicochemical description of the entire process is given in application note MEM4.

2. VOC measurement

Volatile organic compounds (VOCs) are a well-known hazard to human and environmental health[1,2]. In the past years, great effort has been put into monitoring its emissions. Current technologies allow for the detection of the total amount of VOCs (TVOC) but lack the ability of sensitively detecting a specific VOC, i.e. distinguishing acetone from toluene for example. With MEMBRAPOR's innovative VOC electrochemical sensor, TVOC as well as concentrations of individual VOCs can be monitored. Tab. 3 lists some common VOCs with their corresponding CAS number and correction factor. Note that our VOC sensor is not suited for the measurement of aliphatic hydrocarbons (methane, ethane, …).

[1] M.J. Mendell, *Indoor Air*, 17 (4), 259-277 (2007)
[2] J.A. Bernstein et al., *J. Allergy Clin. Immunol*, 121 (3), 585-591 (2008)

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

3. Characteristics of MEMBRAPOR VOC sensor

3.1. Baseline

MEMBRAPOR's VOC sensors can be operated at different bias voltages V_{bias}. Once a sensor is connected to the circuit with a bias voltage or the bias voltage is changed, the sensor's baseline requires between 24 to 72 h to adjust to a new bias voltage. Fig. 1 illustrates the baseline's temporal progress after the electrochemical cell is connected to the potentiostatic circuit with a given bias voltage. When the value of the baseline is constant, the sensor is ready for usage. MEMBRAPOR recommends monitoring the baseline's temporal evolution when the electrochemical cell is i.) connected for the first time into the electronic circuit with a specific V_{bias} or ii.) when V_{bias} is changed. Please note that the value of the baseline can also increase, depending on the current and targeted value of V_{bias}. All sensor leaving the factory are conditioned with a bias voltage of 300 mV.

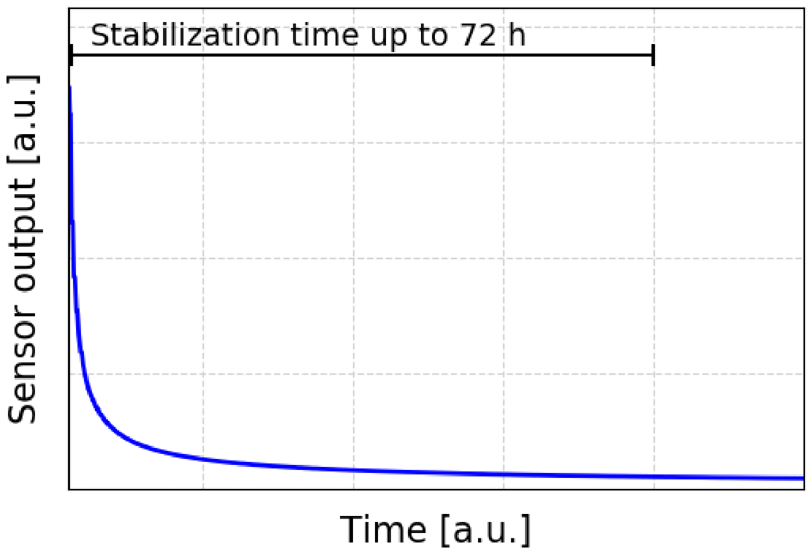

Fig. 1: Temporal evolution of baseline when sensor is connected to circuit with $V_{bias} > 0$ mV.

3.2. Sensor performance

The bias voltage influences the substances' reactivity and therefore three key parameters: the sensitivity, the response time and the recovery time of the sensor. Tab.1 shows typical response and recovery times for a list of substances at different bias voltages. The response time corresponds to t_{90}. A slower recovery time is a result of one or several processes taking place:

- Certain VOCs strongly adsorb on the sensor housing, resulting in a slow release of the substance over time, which is referred to as sponge-effect. Typical observations are a shift in baseline as well as a slow recovery time.

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

- VOC or reaction product partly dissolves in electrolyte resulting in a shift of the baseline.

Generally, after exposure to fresh air the baseline of the sensor recovers to its original level.

V_{bias} [mV]	Response time [s]	Recovery time [s]	Substance
0	< 75	< 90	Formaldehyde
	< 90	< 170	Isopropanol
	< 35	< 60	Xylene
300	< 30	< 15	Formaldehyde
	< 30	< 35	Isopropanol
	< 90	< 200	Xylene
450	< 20	< 120	Formaldehyde
	< 120	< 90	Isopropanol
	< 100	< 200	Xylene

Tab. 1: Response and recovery times of selected substances at V_{bias} = 0, 300 and 450 mV, respectively. The concentrations are 6 ppm Formaldehyde, 42 ppm Isopropanol and 25 ppm Xylene, respectively.

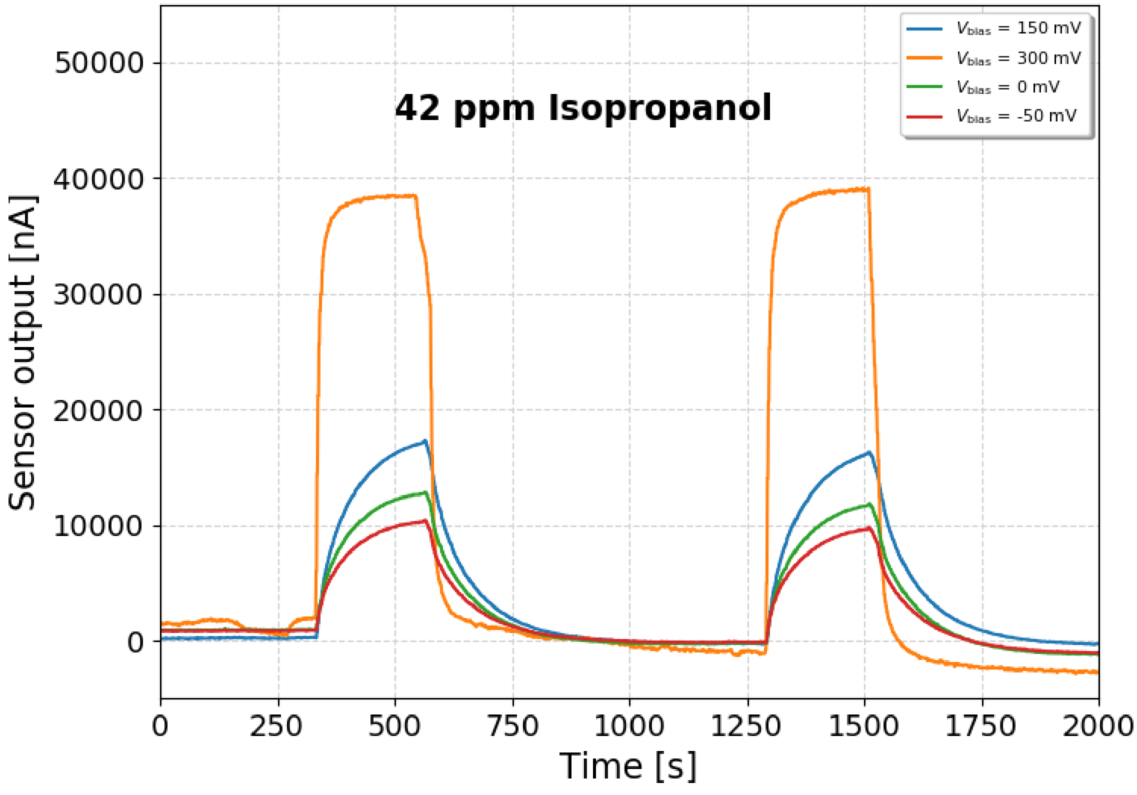

Fig.2: Typical measurement of 42 ppm Isopropanol with VOC sensors at different bias voltages. The traces in ascending bias voltage order: V_{bias} = -50 mV (red trace), V_{bias} = 0 mV (green trace), V_{bias} = 150 mV (blue trace) and V_{bias} = 300 mV (orange trace), respectively.

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

Fig.2 shows a typical measurement with four VOC sensors at four different values of V_{bias}. The measurements illustrate well the effect of the bias voltage on the performance (response time, recovery time and sensitivity) of the sensor unit. The selectivity of the VOC type is further discussed in section 4. Fig.2 also depicts the good reproducibility of the VOC sensor.

3.3. How to use VOC sensor

This section explains how to use the VOC sensor for the measurement of the TVOC. Since every substance has a different sensitivity, evaluation of data and/or calibrations in the field can be quite tedious. Therefore, MEMBRAPOR recommends using Isobutylene (IBE, CAS-Nr. 115-11-7) as a reference substance due to its easy availability, low price, low toxicity and widespread use with other portable VOC detection devices. The relative sensitivity S_{rel} can be expressed with respect to the sensitivity of IBE at V_{bias} = 300 mV ($S_{IBE,300}$) using the following relationship:

$$S_{rel} = \frac{S_{\mathrm{VOC}}}{S_{\mathrm{IBE,300}}} \tag{1}$$

The relative sensitivity is the inverse value of the correction factor CF:

$$CF = \frac{1}{S_{rel}} \tag{2}$$

$$[\text{True VOC concentration ppm}] = CF \cdot [\text{IBE reading ppm}] \tag{3}$$

Therefore, substances with CF > 1 are less sensitive than IBE while substances with CF < 1 are more sensitive than IBE.

Fig. 3 shows the evaluation of measuring a mixture of three substances (here: Isopropanol, Formic acid and Toluene) with the VOC sensor at V_{bias} = 300 mV. The left ordinate indicates the current output *i* for a batch of sensors with its corresponding deviation (black error bars). The light blue bars illustrate the response to 30 ppm Isopropanol, 30 ppm Formic Acid, 18 ppm Toluene and a mixture of all three substances resulting in roughly 80 ppm TVOC. The orange bar shows the sum signal of the response to the individual components. The right ordinate illustrates the sensor output in IBE equivalents (green dots with errors) as calculated based on equations (1) and (2). Thus, the TVOC amount can be expressed as,

$$[\text{ppm IBE}] = \sum_{i=0}^{N} S_{rel,i}[X]_i = \sum_{i=0}^{N} \frac{[X]_i}{CF_i} \tag{3}$$

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

where $[X]_i$ is the concentration of VOC with index i, $S_{rel,i}$ the relative sensitivity and CF_i is the correction factor, respectively. This equation applies if there is no chemical reaction between two VOCs. In Fig. 3 there is a slight difference between the blue bar (label: ~80 ppm TVOC) and the orange bar (label: Sum signal). One reason could be a possible reaction of two VOCs, thus, changing the total concentration.

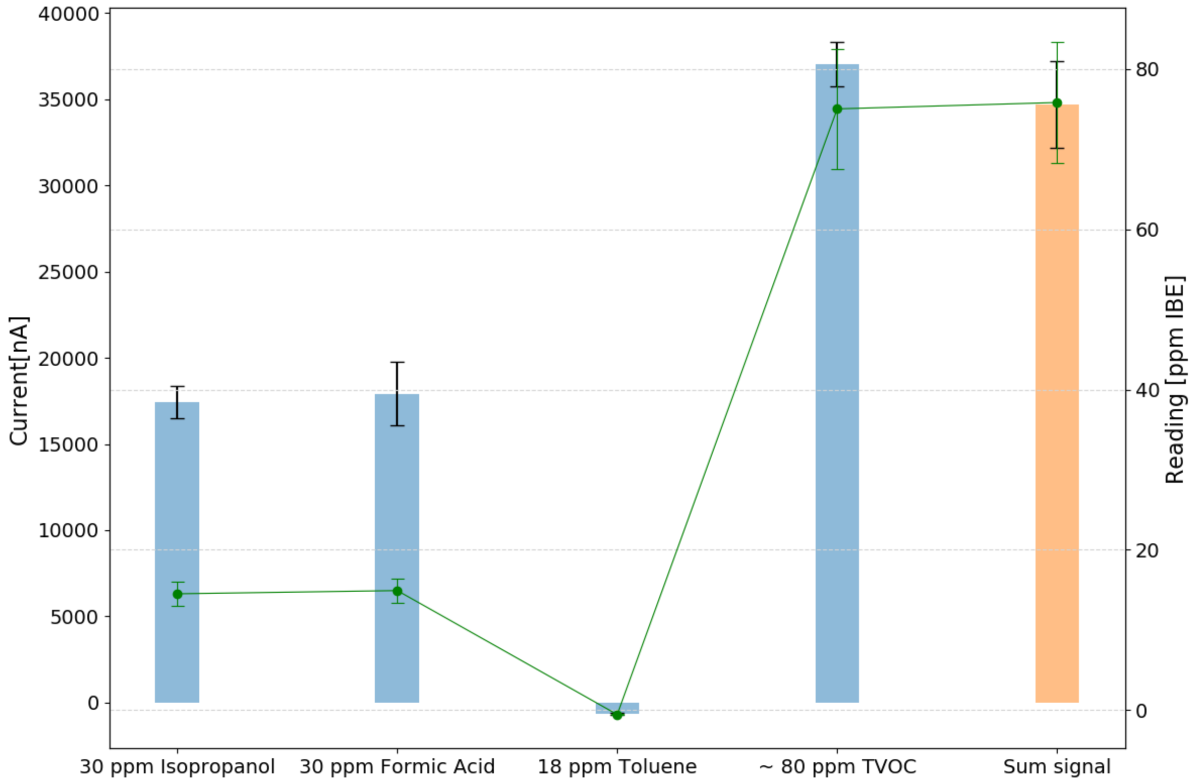

Fig. 3: Bars: Current output of 30 ppm Isopropanol, 30 ppm Formic Acid and 18 ppm Toluene and a mixture of all three substances yielding ~ 80 ppm VOC, respectively. The orange bar indicates the sum signal of the three single components. Points: The green points show the sensor output in IBE equivalents.

4. Selective VOC detection and reactivity curves

The high reactivity of VOCs does not allow for the usual selectivity improvement techniques such as the use of an inboard filter. The use of different bias voltages, however, allows a user to measure a specific VOC with a higher sensitivity in the presence of other substances. The VOC sensors were designed to operate at bias voltages between -600 and 600 mV. With a specific set of bias voltages, it is possible to identify several substances in a mixture using several VOC sensors.

Example for VOC/C-20 (see Tab. *2*): A mixture of 10 ppm Ethylene and 10 ppm Ethylenoxide result in a TVOC signal of 16.7 ppm IBE using eqs. (1) and (3). The signal at a bias voltage of 300 mV is similar for both substances. If the bias voltage is however increased to 450 mV or decreased to 150 mV respectively, the relative reading caused by Ethylene is much higher than the one caused by Ethylenoxide. If

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

the values for the individual sensitivities are known, it is possible to retrieve the concentrations for every individual component with VOC sensors at different bias voltages.

	10 ppm C_2H_4	10 ppm C_2H_4O	TVOC
V_{bias} [mV]	IBE reading @ 300 mV [ppm]		
450	3.7	1.7	5.4
300	10.0	6.7	16.7
150	5.6	1.0	6.6
0	1.3	0.3	1.6
-50	1.2	0.6	1.8

Tab. 2: TVOC signal and individual contributions at different bias voltages for the VOC/C-20. The second and third column show the IBE reading of 10 ppm Ethylene and 10 ppm Ethylenoxide at different bias voltages, respectively. The last column is the total VOC signal in IBE reading.

5. Typical correction factors for common VOC substances

The table below contains a list of typical form factors CF for the VOC/C-20 as determined by Membrapor AG which can be used for guidance. Please note that we strongly recommend determining the form factors directly with your setup since gas sampling plays a pivotal role for VOCs.

Substance	**CAS Nr.**	**Chemical formula**	**CF**	**Remark**
Acetic Acid	64-19-7	$C_2H_4O_2$	60.0	
Acetone	67-64-1	C_3H_6O	< 6.0	1
Benzene	71-43-2	C_6H_6	> 600.0	
Ethylene	74-85-1	C_2H_4	1.0	
Ethylenoxide	75-21-8	C_2H_4O	1.5	
Formaldehyde	50-00-0	CH_2O	0.5	
Formic Acid	64-18-6	CH_2O_2	1.2	
Isobutylene	115-11-7	C_4H_8	1.0	3
Isopropanol	67-63-0	C_3H_8O	1.8	2
Methanol	67-56-1	CH_4O	1.6	
Toluene	108-88-3	C_7H_8	30.0	
Xylene	1330-20-7	C_8H_{10}	9.0	

Tab. 3: List of common VOCs with their corresponding CAS Nr. and CF for the VOC/C-20. The CF listed here is for a bias voltage of 300 mV.

1) Depletion effects in the gas sampling system are very pronounced. The CF depicted in a list is a maximal value; typical values are lower.
2) Long-term exposure can cause slight drifts in the baseline.
3) Reference substance.

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch

6. Appendix

The following section contains the characteristics of for Isobutylene which is used as reference. As explained in section 3.3, all calculations laid out in this document are with respect to the IBE sensitivity recorded at V_{bias} = 300 mV. Fig. 4 shows the sensitivity curve for IBE as a function of the bias voltage. As one can see the reactivity is maximal at voltages of 150 – 300 mV. MEMBRAPOR recommends recording such a reactivity curve with your own device.

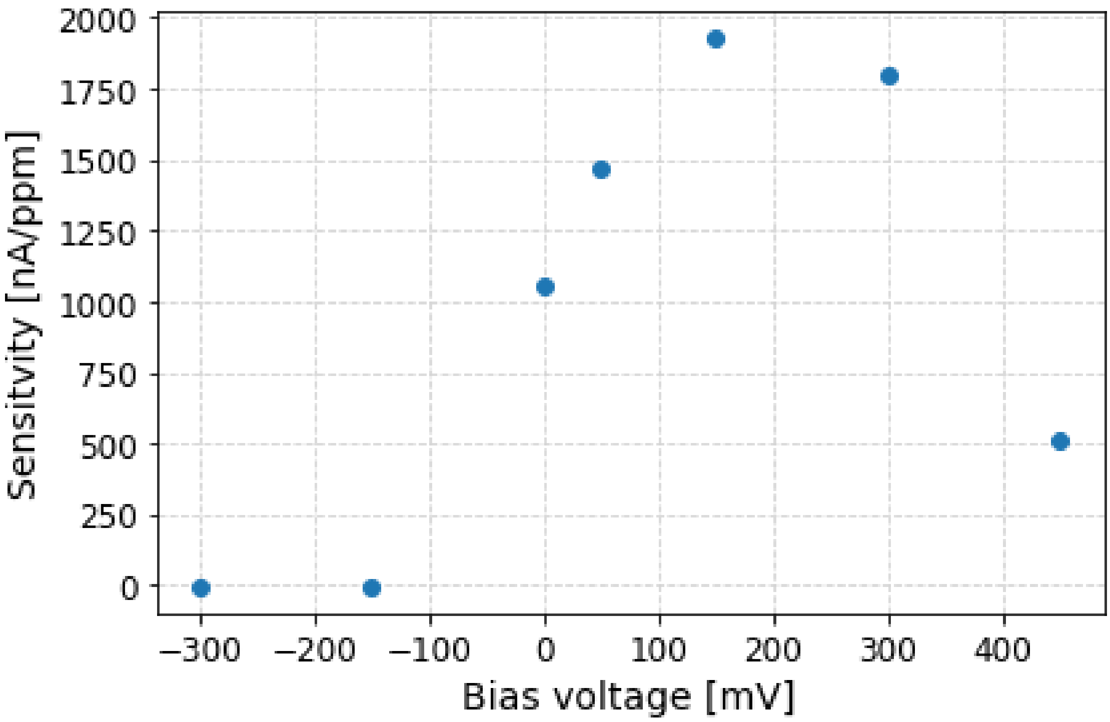

Fig. 4: IBE sensitivity measured at different bias voltages.

Please note that any other substance or bias voltage can be used as a reference point. The data processing works analogously. If you require any assistance, please contact MEMBRAPOR's technical support.

MEMBRAPOR AG, Birkenweg 2, 8304 Wallisellen, Switzerland
Phone +41 43 311 72 00 | Fax +41 43 311 72 01 |
E-Mail: sensor@membrapor.ch | Website: www.membrapor.ch