Supplement of J. Sens. Sens. Syst., 13, 263–275, 2024
https://doi.org/10.5194/jsss-13-263-2024-supplement

JSSS Journal of Sensors and Sensor Systems Open Access

Supplement of

A concept for sensor system developments using raw-milk monitoring as a case study

Maximilian Koehne et al.

Correspondence to: Maximilian Koehne (maximilian.koehne@ivv.fraunhofer.de), Michael Henfling (michael.henfling@emft.fraunhofer.de), and Gina Zeh (gina.zeh@ivv.fraunhofer.de)

S1. Temperature program for GC measurements

Helium was used as standard carrier gas. Flow rates and temperature programs for each measurement are depicted in table S1.

Table S1: Temperature programs for GC measurements with different flow rates and columns.

(a) Temperature program for GC-O measurements on DB-FFAP column.

Flow [ml/min]	Ramp [° C/min]	Temperature [° C]	Hold time [min]
2,5		40	2
	10	240	5

(b) Temperature program for GC-O measurements on DB-5 column.

Flow [ml/min]	Ramp [° C/min]	Temperature [° C]	Hold time [min]
		35	5
2,5	6	100	0
	10	300	10

(c) Temperature program for GC-MS measurements on DB-FFAP column.

Flow [ml/min]	Ramp [° C/min]	Temperature [° C]	Hold time [min]
1		40	2
	8	240	10

(d) Temperature program for GC-MS measurements on DB-5 column.

Flow [ml/min]	Ramp [° C/min]	Temperature [° C]	Hold time [min]
		35	5
1	6	200	0
	10	300	10

S2. PTR-MS

Calibration

For the purpose of calibration, an advanced liquid calibration unit (LCU-a, Ionicon Analytik GmbH, Innsbruck, Austria) was coupled to a PTR-TOF-MS 8000 (Ionicon Analytik GmbH, Innsbruck, Austria). The latter operated at the same settings as for sample analysis. The main principle of a LCU is to generate a gas stream containing compounds at known volume mixing ratios by evaporating liquid standards. Further details are described elsewhere (Fischer et al., 2013). Aqueous standards of ethanol (4.48 mg/L), acetic acid (7.04 mg/L), ethyl acetate (8.80 mg/L), pentan-1-ol (8.68 mg/L), 3-methylbutan-1-ol (8.74 mg/L) and hexan-1-ol (9.68 mg/L) were prepared and, respectively, attached to the first LCU pump. Deionized water was attached to the second pump. Via a nebulizer, operating with a gas flow (filtered air) of 1000 sccm, each standard solution was transferred into a heated (110 °C) evaporation chamber with a total liquid flow rate of 50 µl/min. Initially, a blank sample (H_2O) was measured. After measuring a standard solution for 10 min at full flow rate (50 µl/min), the flow rates of both pumps were modified to achieve stepwise dilutions (80 %, 60 %, 40 %, 20 %) to achieve gas-phase concentrations of about 20–100 ppb, which were measured for 5 min each. Ethanol, acetic acid and ethyl acetate were calibrated via their mass to charge ratio (*m/z*) of the molecular ions with *m/z* 47.049, *m/z* 61.028, and *m/z* 89.060, respectively, whereas the other compounds were calibrated via fragment ions, namely *m/z* 57.070 for hexan-1-ol, and *m/z* 71.086 for both 3-methylbutan-1-ol and pentan-1-ol. The signal intensities in counts-per-second (cps) were corrected by the *m/z*-specific transmission within the PTR-time of flight MS (TOFMS) instrument and normalized to the primary ion signal (*m/z* 21.022, multiplier 500) with a normalization factor of 10^7 to obtain normalized count-rates (ncps). Plotting the mean signal intensities (ncps) of each dilution versus the gas-phase concentrations resulted in sensitivity factors and correlation coefficients (R^2) of 4.73 (R^2 = 0.9990), 4.77 (R^2 = 0.9994), 41.0 (R^2 = 0.9994), 4.91 (R^2 = 0.9991), 4.45 (R^2 = 0.9997), and 4.25 ncps/ppb (R^2 = 0.9988) for ethanol, hexan-1-ol, acetic acid, 3-methylbutan-1-ol, pentan-1-ol, and ethyl acetate, respectively.

Detection and quantification limits

For each compound, the limit of detection (LOD) was determined by multiplying the mean standard deviation (SD) of blank signals (ncps) in a 5-fold determination by 3. The limit of quantification (LOQ) was calculated by multiplying the LOD by 3.3. This resulted in LOD/LOQ values of 41.3/136, 58.5/193, 86.3/285, 32.6/108, and 17.9/59 ncps for *m/z* 47.049 (ethanol), *m/z* 57.070 (hexan-1-ol), *m/z* 61.028 (acetic acid), *m/z* 71.086 (3-methylbutan-1-ol and pentan-1-ol), and *m/z* 89.060 (ethyl acetate), respectively.

An overview of the measurement results of all raw milk samples is shown in Figure 1 and Table 5.

Results for single measurements of all raw milk samples:

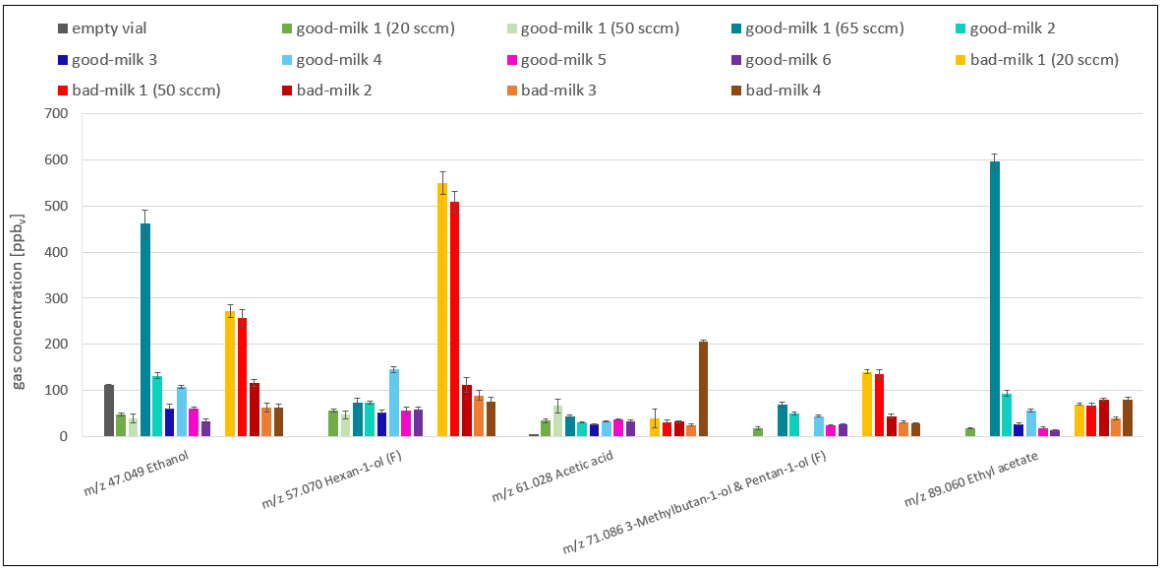


Figure S1: PTR-MS measurements of an empty vial and quintets for all raw milk samples. Shown are mean values with standard deviation for each sample. Aspiration rate was at 20 sccm and 50 sccm for the first measurement day and at 65 sccm for the second measurement day. If not explicitly mentioned, the rate was at 65 sccm. F stands for detected ion fragment.

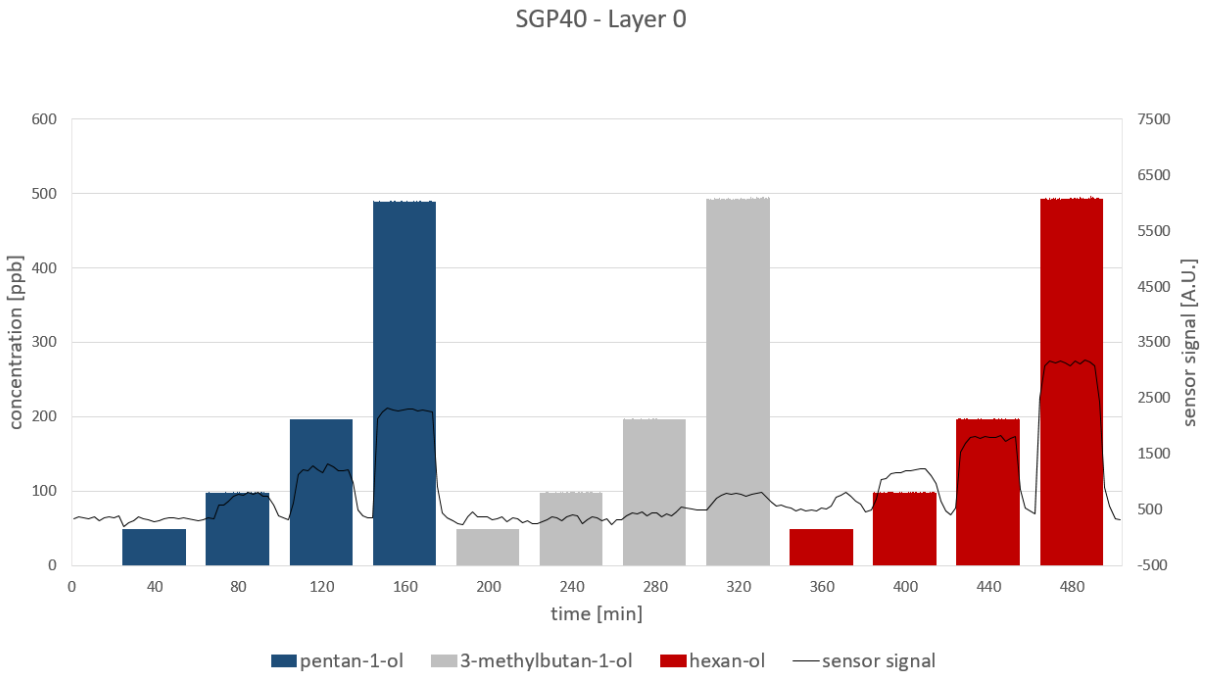
Table S2: Measured concentration of quintets for each milk sample in ppb with PTR-MS. F stands for detected ion fragment.

Sample	m/z 47.049 Ethanol		m/z 57.070 Hexan-1-ol (F)		m/z 61.028 Acetic acid		m/z 71.086 3-Methylbutan-1-ol & Pentan-1-ol (F)		m/z 89.060 Ethyl acetate	
	mean [ppb]	SD [ppb]	mean [ppb]	SD [ppb]	mean [ppb]	SD [ppb]	mean [ppb]	SD [ppb]	mean [ppb]	SD [ppb]
empty vial	112.4	0.0	-	-	4.7[a]	0.0	-	-	-	-
good-milk 1 (20 sccm)	48.6[a]	3.5	56.7[a]	2.5	34.4	4.0	17.6[a]	2.7	18.4[a]	1.7
good-milk 1 (50 sccm)	39.2[a,b]	9.4	47.2[a]	8.1	66.9	14.8	-	-	-	-
good-milk 1 (65 sccm)	461.1	29.2	74.4[a]	8.4	43.4	2.8	69.1[a]	4.8	597.1	16.2
good-milk 2 (65 sccm)	132.1	6.6	73.9[a]	3.2	31.3	0.6	49.7[a]	3.3	93.6	6.5
good-milk 3 (65 sccm)	61.7[a]	9.2	52.4[a,b]	6.2	25.9	1.8	-	-	25.8[a]	3.7
good-milk 4 (65 sccm)	107.7[a]	3.5	145.2[a]	7.2	34.0	1.1	43.9[a]	2.2	56.3[a]	3.7
good-milk 5 (65 sccm)	60.6[a]	2.8	55.8[a]	7.8	37.2	0.8	24.8[a,b]	1.3	18.6[a]	1.9
good-milk 6 (65 sccm)	32.1[a]	6.2	59.0[a]	4.5	33.2	2.7	27.1[a,b]	-	13.4[a]	2.2
bad-milk 1 (20 sccm)	272.5	14.0	548.6	24.6	39.1	20.4	140.8	4.3	69.3	2.1
bad-milk 1 (50 sccm)	256.8[a]	17.4	509.6	22.3	31.9	4.1	135.3[a]	10.3	67.7[a]	3.9
bad-milk 2 (65 sccm)	116.8	7.4	112.1[a]	16.5	32.4	2.1	44.1[a]	4.1	79.7	4.0
bad-milk 3 (65 sccm)	63.2[a]	9.9	89.2[a]	10.1	25.0	1.7	31.0[a]	2.1	39.2[a]	4.0
bad-milk 4 (65 sccm)	62.6[a]	8.2	75.9[a]	9.4	205.1	3.6	27.8[a]	2.0	80.4	3.9

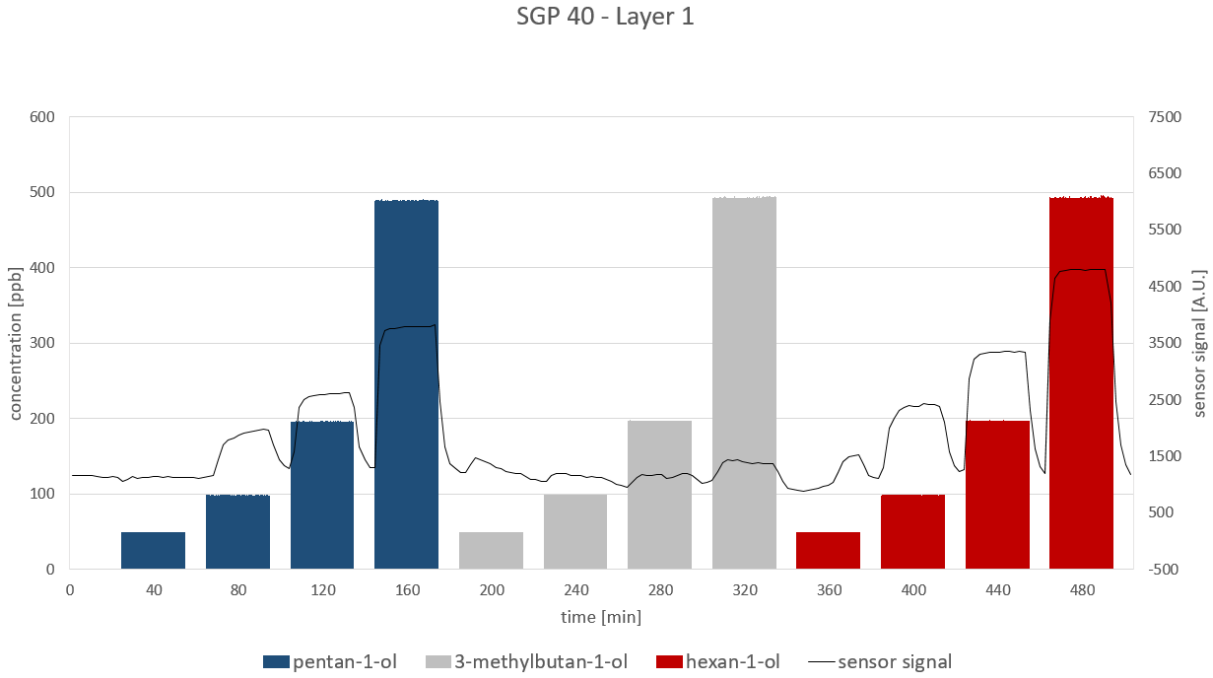
[a]at least one measurement of the 5-fold determination was below LOQ
[b]at least one measurement of the 5-fold determination was below LOD and therefore not considered
- values not considered, as all values are below LOD

S3. Sensor response of all four layers in the quasi-static signal (exemplarily)

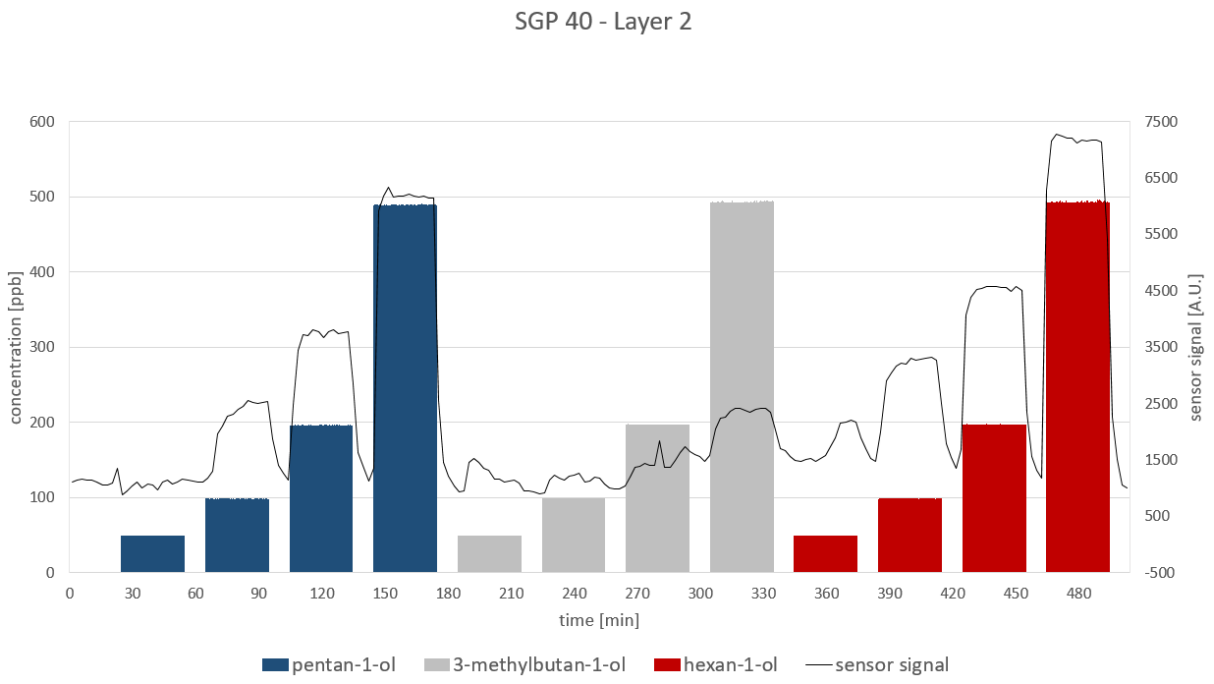
(a)



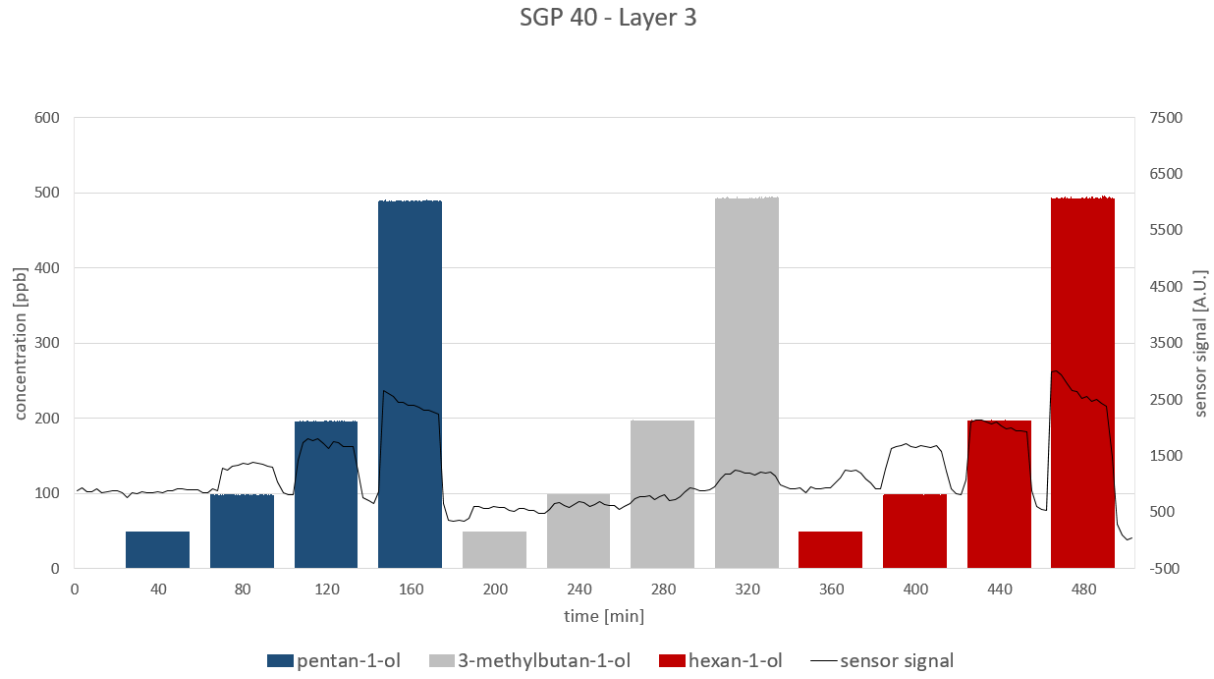
(b)



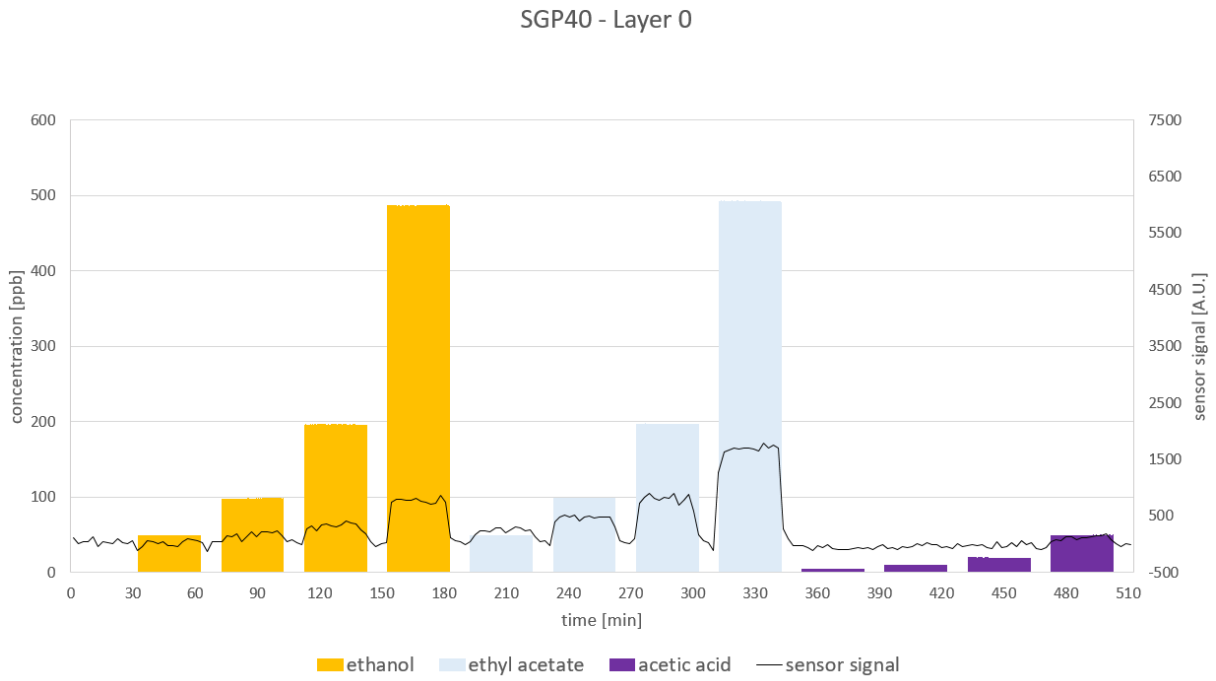
(c)


SGP 40 - Layer 2
concentration [ppb]
sensor signal [A.U.]
time [min]
pentan-1-ol
3-methylbutan-1-ol
hexan-1-ol
sensor signal

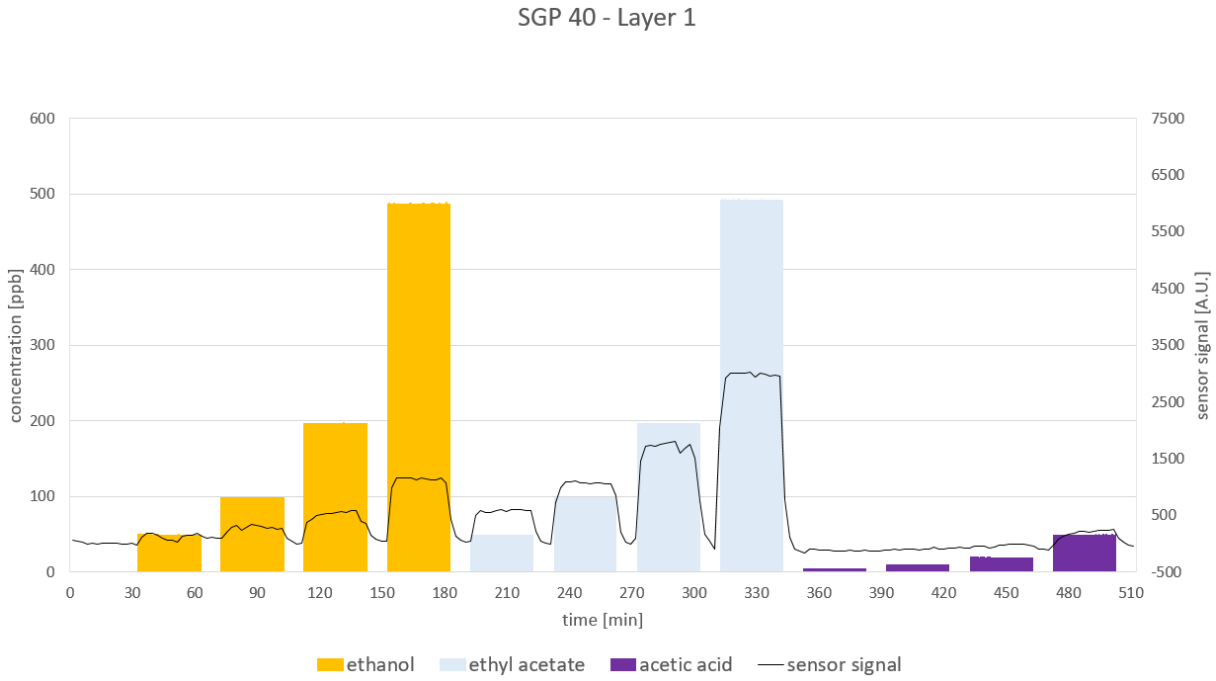
(d)


SGP 40 - Layer 3
concentration [ppb]
sensor signal [A.U.]
time [min]
pentan-1-ol
3-methylbutan-1-ol
hexan-1-ol
sensor signal

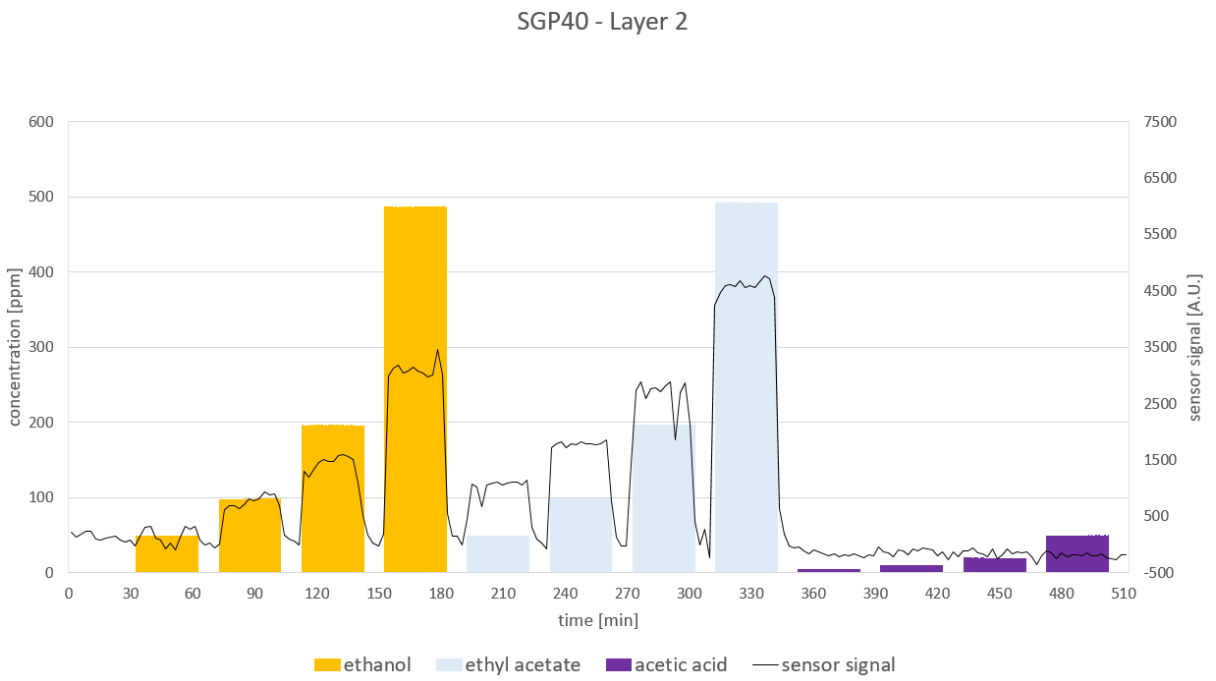
(e)


SGP40 - Layer 0
concentration [ppb]
sensor signal [A.U.]
time [min]
ethanol
ethyl acetate
acetic acid
sensor signal

(f)


SGP 40 - Layer 1
concentration [ppb]
sensor signal [A.U.]
time [min]
ethanol
ethyl acetate
acetic acid
sensor signal

(g)



(h)

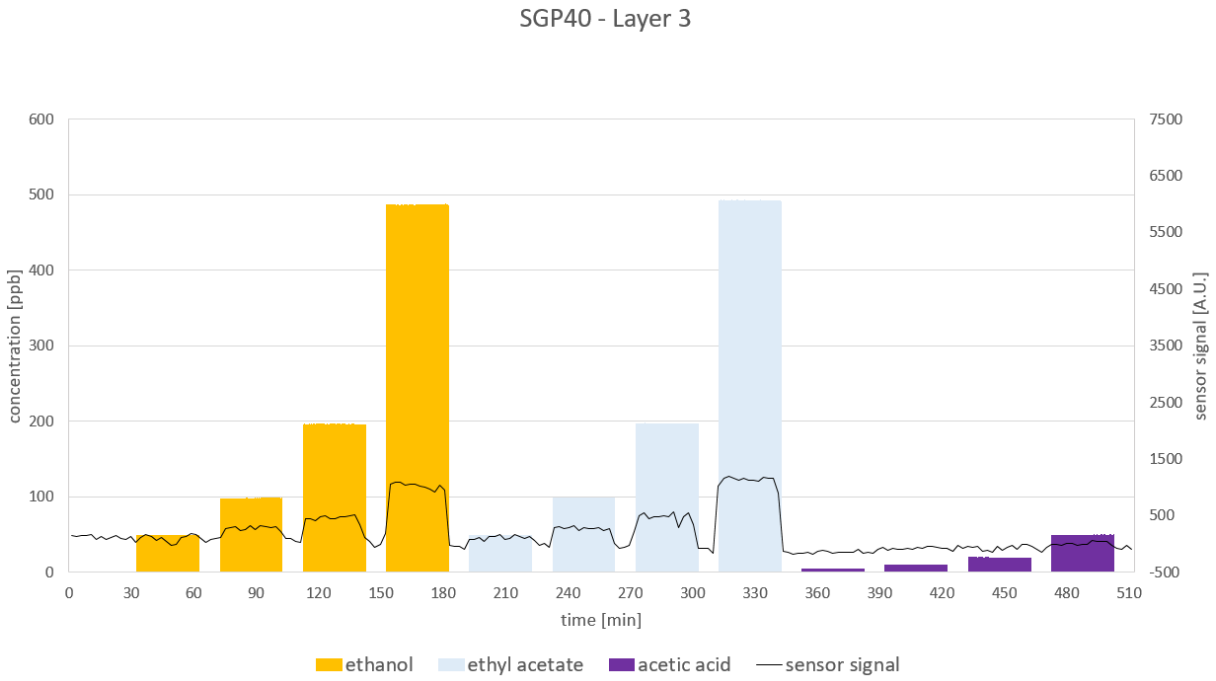


Figure S2: Sensor signal at the randomly chosen set point of 105 seconds within the temperature cycle from all four layers (0-3) of the SGP40 for potential markers. (a) Layer 0 with pentan-1-ol, 3-methylbutan-1-ol, hexan-1-ol; (b) Layer 1 with pentan-1-ol, 3-methylbutan-1-ol, hexan-1-ol; (c) Layer 2 with pentan-1-ol, 3-methylbutan-1-ol, hexan-1-ol; (d) Layer 3 with pentan-1-ol, 3-methylbutan-1-ol, hexan-1-ol; (e) Layer 0 with ethanol, ethyl acetate and acetic acid; (f) Layer 1 with ethanol, ethyl acetate and acetic acid; (g) Layer 2 with ethanol, ethyl acetate and acetic acid; (h) Layer 3 with ethanol, ethyl acetate and acetic acid.

S.4 Sensor response of the BME688

The BME 688 sensor was left running during the measurement period to monitor the parameters pressure (Figure 3), humidity (Figure 4) and temperature (Figure 5) in the sensor chamber. In time period five, there is a fluctuation between hour 66 and hour 68 for both pressure and humidity. Graph five is therefore scaled differently for the pressure than the other graphs. This fluctuation is due to the replacement of a container at the GMA, which opened the system for a short time. No other variations were observed and a constant course of all three parameters during the measurements could be shown.

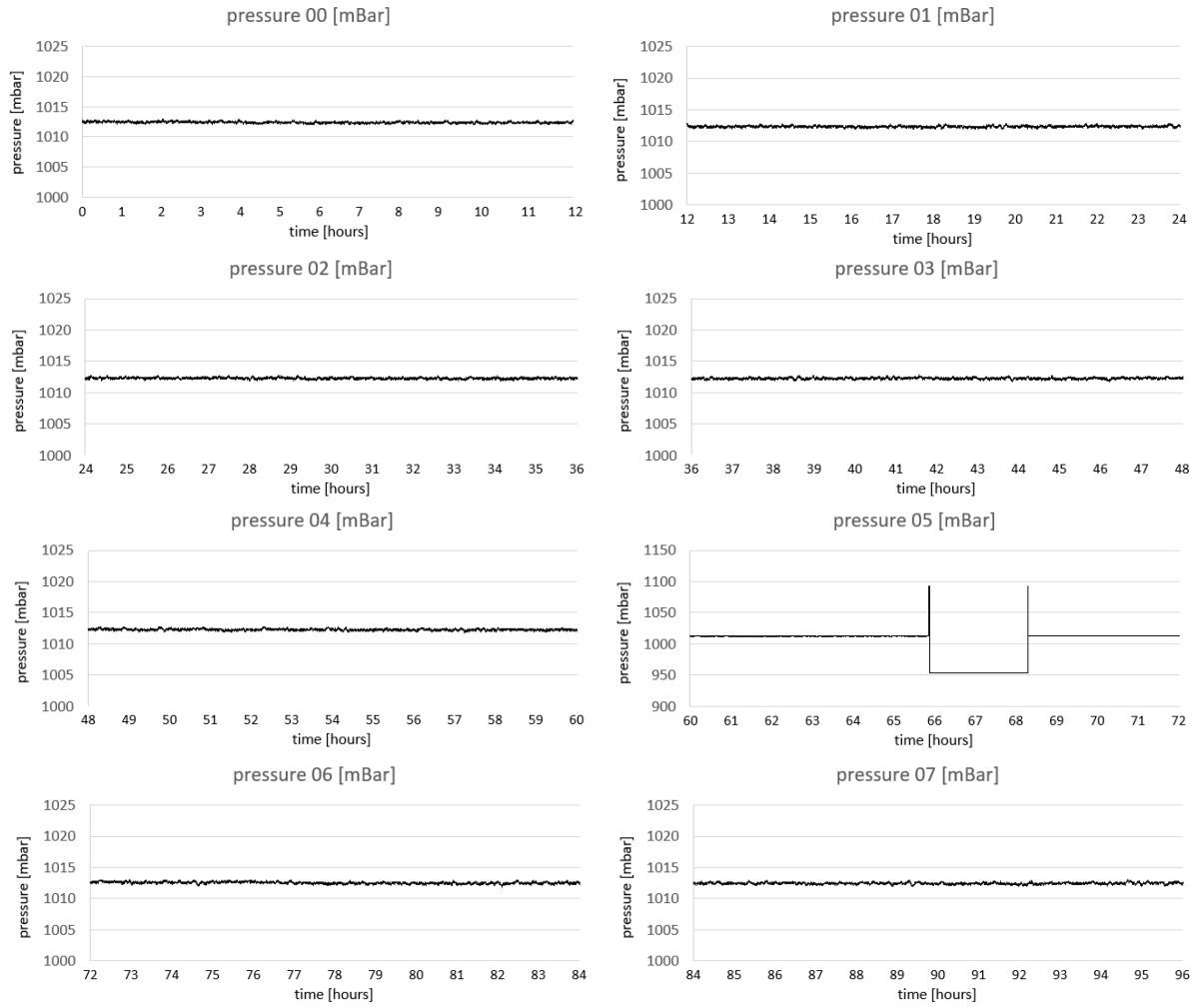


Figure S3: Pressure within the sensor chamber during experiments.

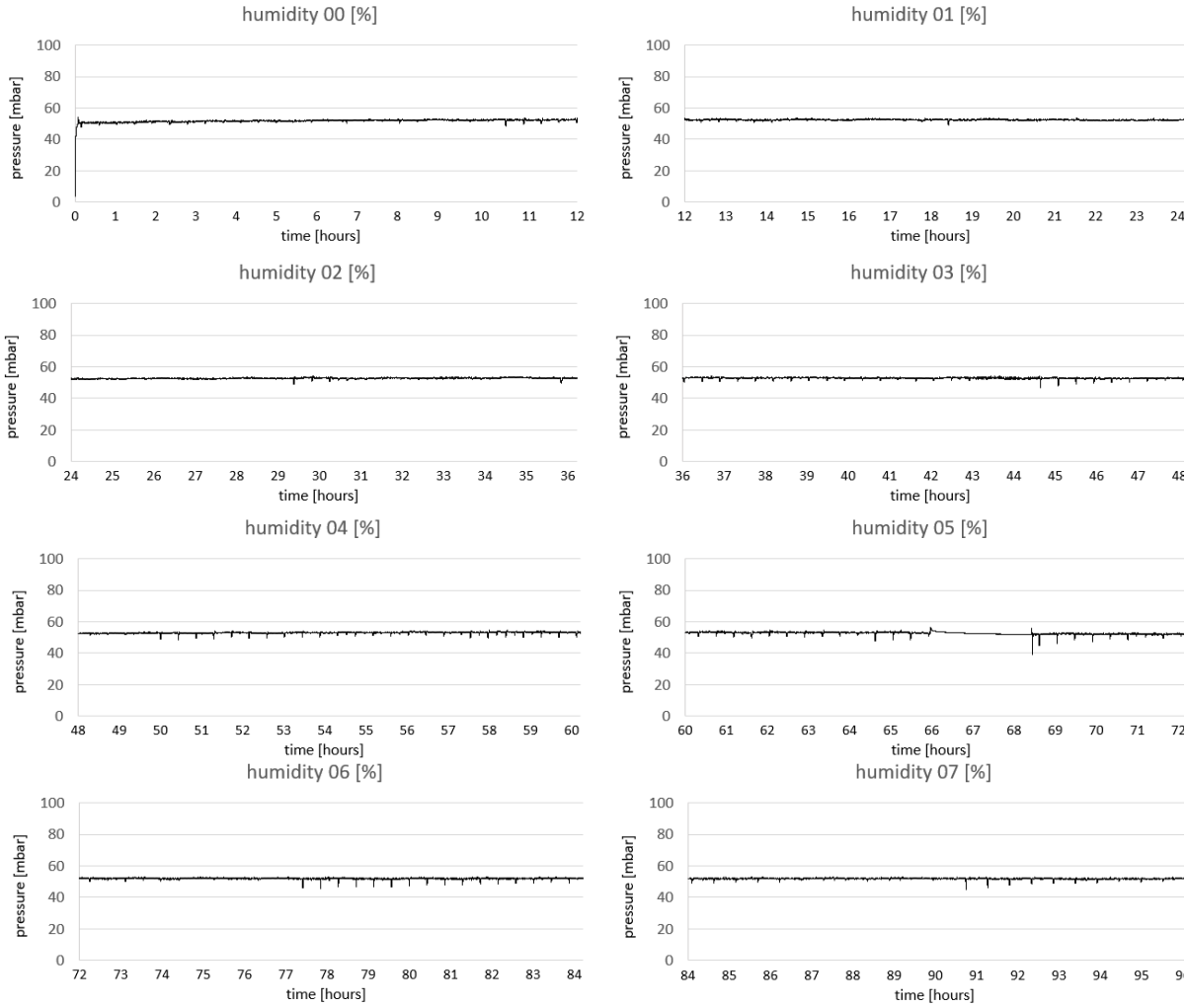


Figure S4: Humidity within the sensor chamber during experiments.

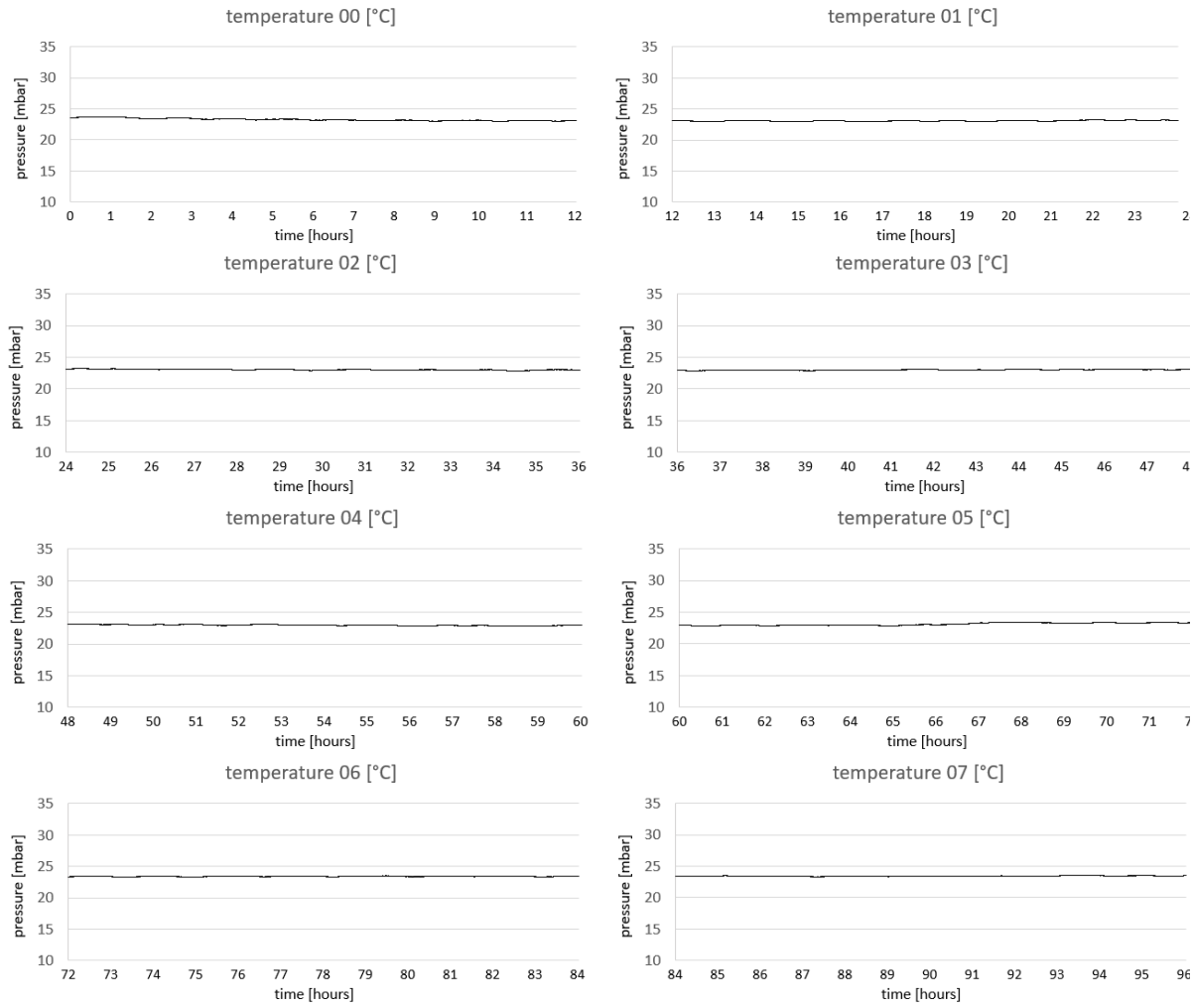


Figure S5: Temperature within the sensor chamber during experiments.

S5. Performance of the quantification models

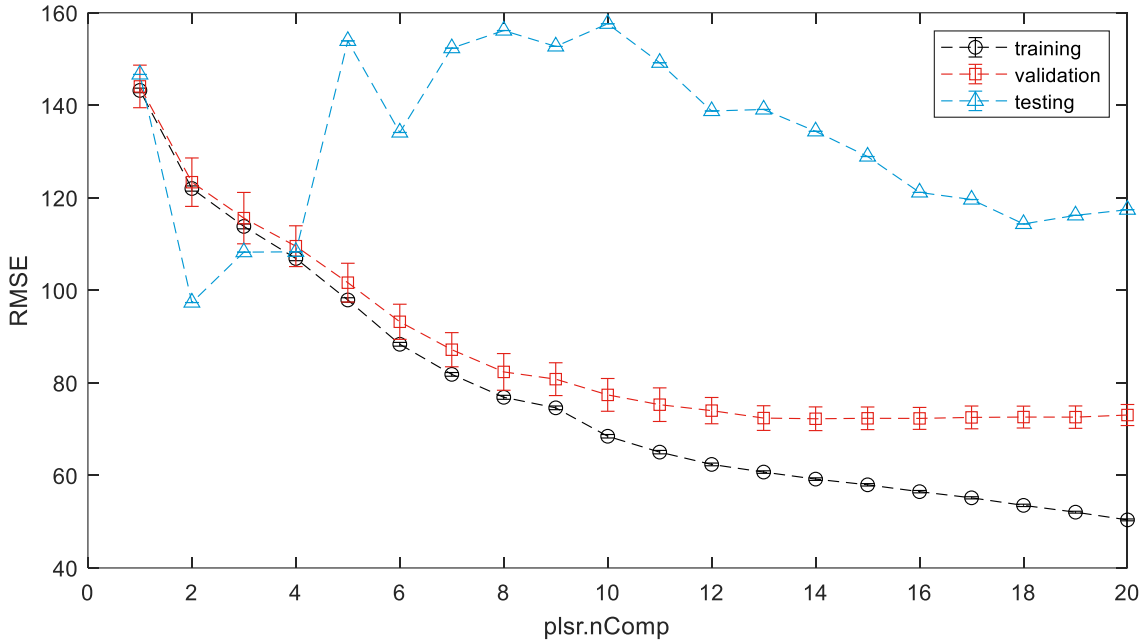


Figure S6: Performance of the model with all alcoholic markers for 1 to 20 PLSR components.

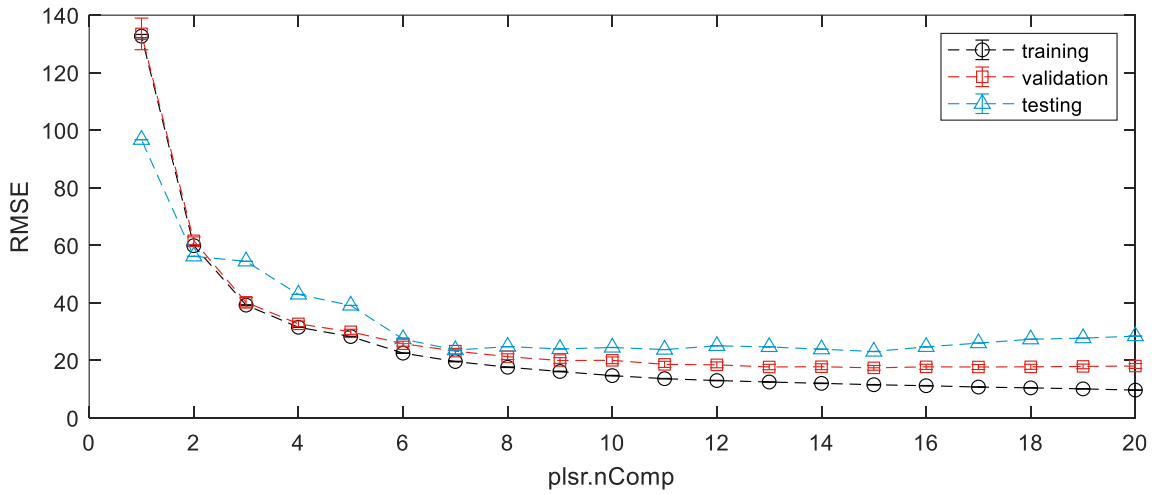


Figure S7: Performance of the model excluding 3-methyl-1-butanol for 1 to 20 PLSR components.