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Field evaluation of low-cost electrochemical air quality gas sensors under extreme temperature and relative humidity conditions

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S.1 Technical information of sensors utilised

Table S1: Specifications of the Alphasense and Winsen low-cost gas sensors employed in our study.

	Alphasense CO-B41 [1]	Alphasense NO_2-B43F [2]	Alphasense SO_2-B4 [3]	Alphasense OX-B431 [4]	Winsen ZE12(A) [11]	
					ZE12(A)-O_3 ZE12(A)-SO_2 ZE12(A)-NO_2	ZE12(A)-CO
Detection Range (ppm)	1000	20	100	20	2	12.5
Operating Temperature range (°C)	-30 to 50	-30-40	-30 to 50	-30 to 40	-20 to 50	-20 to 50
Operating Humidity range (%RH)	15 to 90	15 to 85	15 to 90	15 to 85	15 to 90	15 to 90
Response time (s)	< 25 (from 0 to 10ppm)	<60 (from 0 to 2ppm)	< 60 (from 0 to 2ppm)	< 60 (from 0 to 1ppm)	≤120	≤120
Noise[1] ±2 standard deviations (ppb) – theoretical detection limit	4	15	5	15	~15 (O_3) ~11 (SO_2) ~16 (NO_2)	~129
Cross sensitivity gas	H_2S	O_3 - Cl_2	NO_2 - Cl_2 O_3 - CO	Cl_2 - H_2S	-	-
Sensitivity from 20°C to 50 °C / zero current (nA)	-50 to -200	-10 to 50	10 to 30	5 to 100	-	-
Lifespan	>36 months operation until the loss of 50% of the original signal (24 months warranted)	>24 months operation until the loss of 50% of the original signal (24 months warranted)	>36 months operation until the loss of 50% of the original signal (24 months warranted)	>24 months operation until the loss of 50% of the original signal (24 months warranted)	2 years (in air)	2 years (in air)
Dimensions (mm)	Ø32 x 16.5	Ø32 x 16.5	Ø32 x 16.5	Ø32 x 16.5	Ø39 x 44	Ø39 x 44
Weight (g)	<13	<13	<13	<13	75	75
Cost with ISB (€)	134	139	134	144	-	-

[1] Tested with Alphasense ISB low noise circuit.

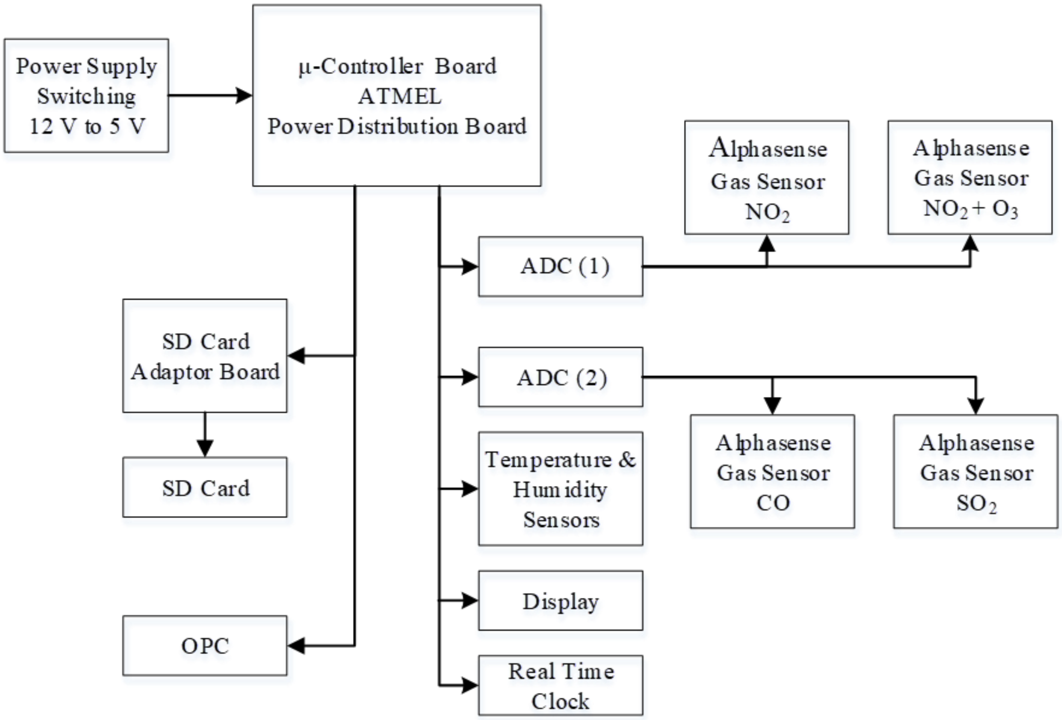

Figure S1: Schematic diagram of the circuit employed for running and recording the data of the LCSs in our study. Key: OPC, Optical particle counter; ADC: Analogue to Digital Converter.

Table S2: Type and specifications of the reference instruments employed at the air quality monitoring station used for the field tests.

	CO	NO_2	O_3	SO_2
Model Method	Ecotech Serinus 30 infrared spectroscopy [7]	Ecotech Serinus 40 Chemiluminescence [8]	Thermo Scientific 49i ultraviolet photometry [10]	Ecotech Serinus 50 ultraviolet fluorescence [9]
Sample flow rate	1.0 slpm	0.3 slpm (0.6 slpm total flow for the NO and NOX flow path)	1–3 LPM	0.750 slpm
Precision	20 ppb or 0.1% of reading, whichever is greater	0.4 ppb otherwise 0.5% of reading, whichever is greater	–	0.5 ppb or 0.15 % of reading, whichever is greater
Linearity	Better than ±1% of full scale (0-50 ppm); ±2% of full scale (0-200 ppm), from best straight-line fit	±1% of full scale	± 1% of full-scale	±1 % of full scale (from best straight-line fit)
Response time	60 seconds to 95%	15 seconds to 90%	20 seconds (10 seconds lag time)	60 seconds to 95 %
Lower detectable limit (ppb)	40	0.4	1.0	0.3

Table S3: Temperature correction factors used in Eq. 1 and 2 in the main manuscript. [5]

Sensor	Equation	Factor	Temperature (°C)								
			-30	**-20**	**-10**	**0**	**10**	**20**	**30**	**40**	**50**
CO-B4	1	n_T	0.7	0.7	0.7	0.7	1	3	-3.5	-4	4.5
NO2-B43F	2	k_T	2.2	2.2	2.2	2.2	1.7	1	0.7	0.3	-2.5
OX-B431	1	n_T	0.9	0.9	1	1.3	1.5	1.7	2	2.5	3.7
SO2-B4	2	k_T	1	1	1	1	1	1	1.2	1.9	3.6

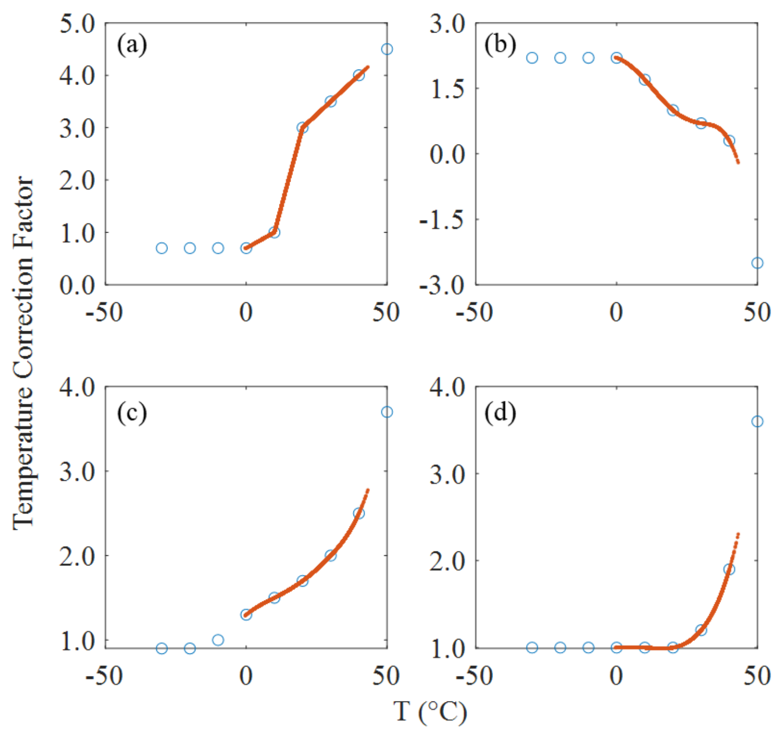

Figure S2: Linear and spline interpolations used for estimating the correction factors of the CO (a) NO_2 (b), O_3 (c) and SO_2 (d) Alphasense LCSs.

S.2 Relative errors of LCSs against reference concentrations

Figure S3 shows that the relative error of LCSs increases exponentially as the nominal gas concentration decreases. Also a sharp increase in the relative error is observed the further we move bellow the LoD of CO, NO_2 and O_3 LCSs as this is defined by the manufacturers (cf. dashed vertical lines in each plot). The relative error of the Alphasense CO LCS (Figure S3a) decreases as the reference concentration increases and reverses to negative error values (indicated by the red data points in all the plots), underestimating the reference concentrations above a certain threshold (ca. 200 ppb). Same behaviour is observed for Winsen CO sensor (Figure S3e) which starts underestimating the reference concentrations when those are above ca. 500 ppb. Both CO LCSs reach a plateau at concentrations > 1000 ppb where the relative error is ca. 65%. The Alphasense NO_2 LCS (Figure S3b) mostly overestimate the reference concentration while the Winsen LCS (Figure S3f) start underestimating at a concentration comparable to its LoD. The Alphasense O_3 LCS (Figure S3c) mostly overestimate while the Winsen (Figure S3g) underestimate the reference measurements. The SO_2 measurements of both LCSs (Figure S3d and S3h) were admittedly higher than the reference measurements, and as discussed in the main manuscript the associated errors can be attributed to the fact that the concentrations of the gas were almost always below the LoD of the sensors, preventing any further evaluation of their performance.

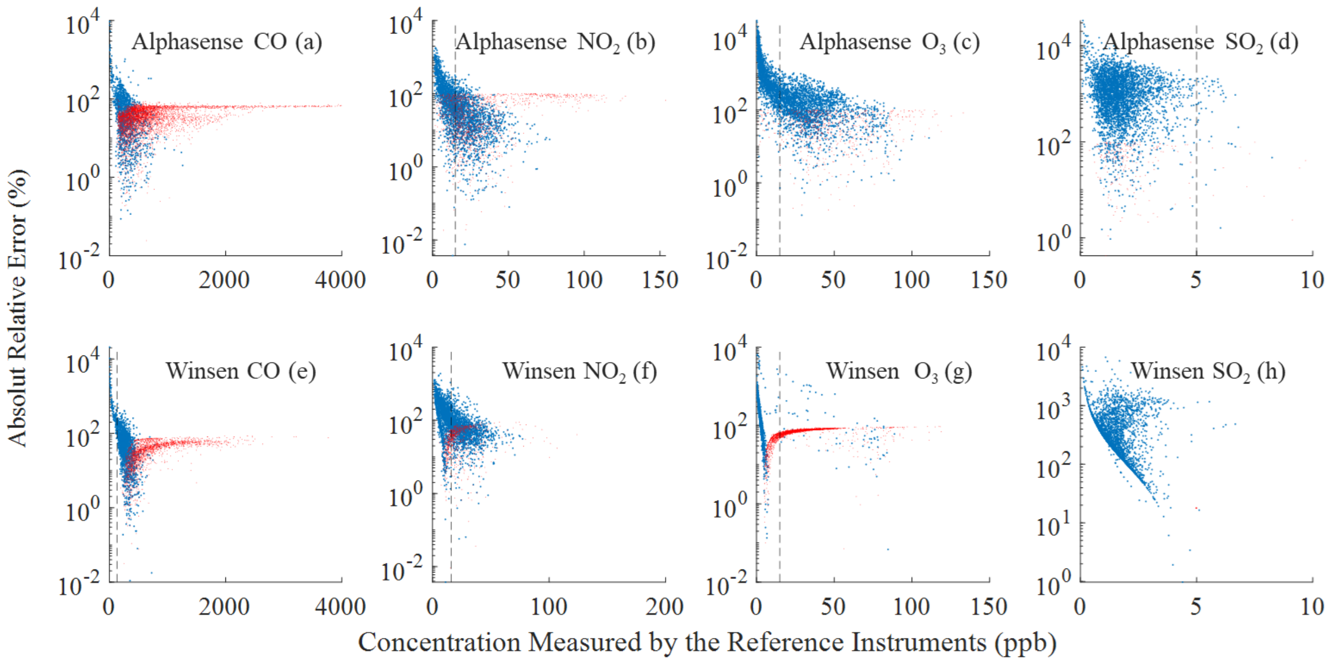

Figure S3: Absolute relative error of the measurements reported by the Alphasense (1st row) and the Winsen (2nd row) LCSs against reference measurements. Blue and red data points correspond respectively to positive and negative relative errors on an absolute scale. Vertical dashed lines indicate the limit of detection (LoD) of each LCS. The LoD values of the Alphasense CO and the Winsen SO_2 LCSs are respectively 4 and 15 and can thus not be visible in the respective subplots.

S.3 CO LCSs Correlation plots tagged by time

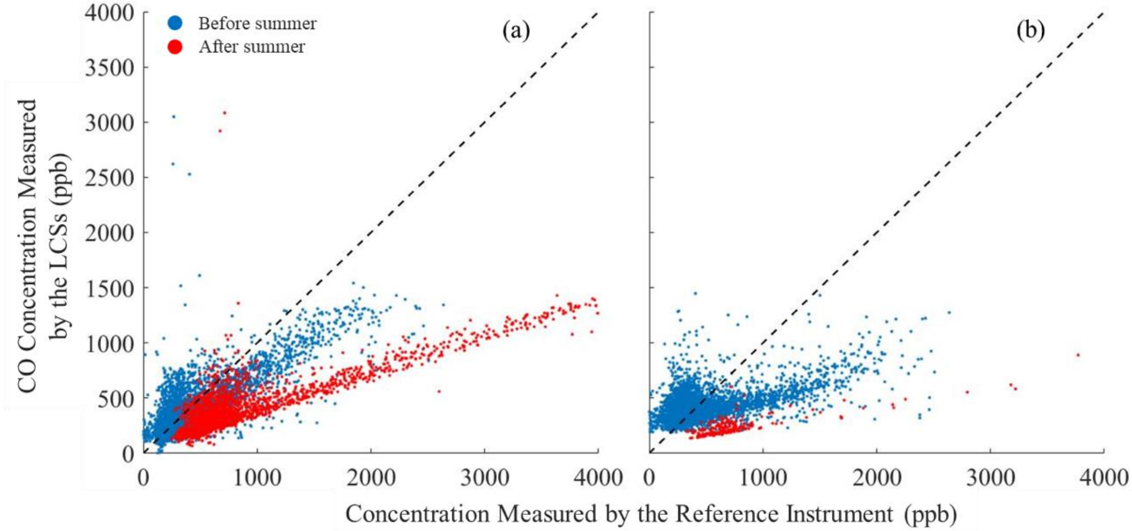

Figure S4: Correlation between the measurements recorded by the Alphasense (a) and Winsen (b) CO LCSs and those provided by the respective reference instrument. Blue and red data points indicate measurements carried out before and after the summer period, whereas the dashed lines are the 1:1 line. The two distinct data clusters (red and blue) formed for both sensors are largely due to the degradation of the sensors by their extended exposure to high temperature and low relative humidity conditions.

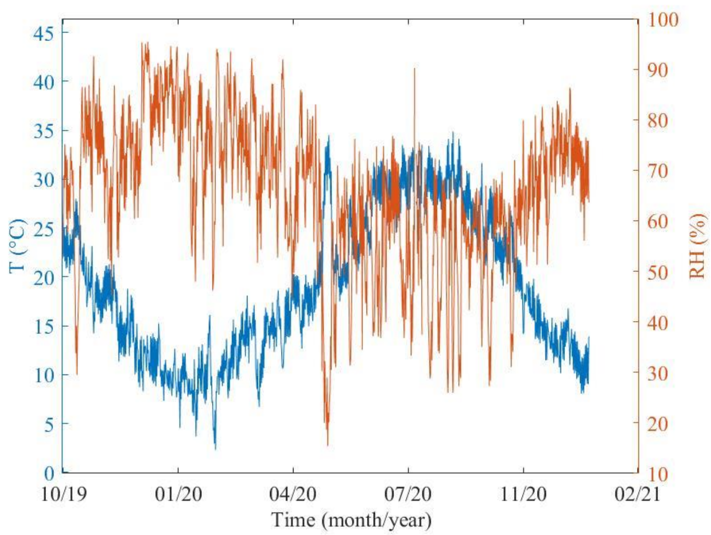

Figure S5: Time series of 12-hour averaged temperature and Relative Humidity (RH) conditions measured by the reference instruments for the period under study.

S.4 Alphasense O_3 LCS correction for NO_2

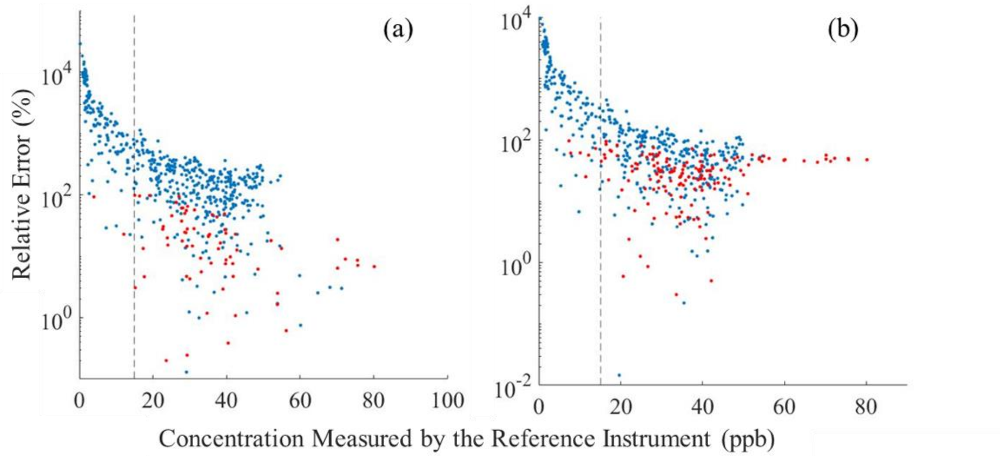

Figure S6: Relative error of the Alphasense O_3 LCS as a function of the respective reference measurements, when (a) NO_2 compensation factor ($WE_{C_{NO2}}$) was subtracted from the calibration equation (i.e., Eq. 1 in the main manuscript) as suggested by the manufacturer, and (b) when this was not done (i.e. using Eq. 1 without subtracting the NO_2 response). Temperature and RH were chosen to be in the range of 10-20 °C and 55-75%, respectively. The vertical dashed line shows the LoD of the LCS. Blue and red coloured points indicate respectively positive and negative relative errors on an absolute scale. The range of relative error changes from -200 to 1000% when the correction for NO_2 cross sensitivity is used, to -100 to 200% when it was not.

S.5. Data Quality Objectives

Table S4 provides the EU AQ standards for the gases considered in this work. The averaging period of each gas differs as those are related to health impacts depending on exposure time. Table S4 also indicates whether the LoD values of the LCSs, are sufficient according to the guideline standards (first point discussed in Section 3.5 of the main manuscript). Evidently, all LCSs have LoD values below the guideline standard.

Table S4: EU guideline standard concentrations, according to Directive 2008/50/EC [6], for the gases investigated in our work, and LoDs of the LCSs we employed.

Gas	EU guideline standard concentration	Averaging Period	Limit of Detection (LoD)	
			Alphasense	Winsen
CO	10 mg/m3 (~8621 ppb)	Maximum daily 8 hour mean	4 ppb	130 ppb
NO_2	200 µg/m3 (~105 ppb)	1 hour	15 ppb	15 ppb
O_3	120 µg/m3 (~60 ppb)	Maximum daily 8 hour mean	15 ppb	15 ppb
SO_2	350 µg/m3 (~132 ppb)	1 hour	5 ppb	15 ppb

Time coverage is defined as the fraction of a calendar year during which sampling shall be in operation. In order to calculate the time coverage of the LCSs based on our dataset we used the following formula:

$$\text{Time coverage} = \frac{N_{meas}}{N_{year}}. \quad \text{(S1)}$$

Here N_{meas} is the number of hours that measurements take place, and N_{year} is the total number of hours in the calendar year. According to the regulations, N_{meas} include invalid measurements, regardless of the cause (e.g., maintenance or malfunction) while for indicative measurements of O_3, time coverage is calculated only for the summer season (April – September). Data capture is defined as the fraction of valid measurements over the required number of hours that measurements have to be carried out (i.e., as required by the time coverage objective, Table S6). The data capture is determined as:

$$\text{Data capture} = \frac{N_{valid}}{(N_{year} \times t_{Min\_Cov})}, \quad \text{(S2)}$$

where N_{valid} is the number of valid hourly/daily measurements in the measurement period, and t_{Min_Cov} is the minimum time coverage requirement.

Table S5: Minimum data capture and time coverage requirements, and indication of whether these are met by LCSs used in our study for indicative measurements.

Gas	LCS	Required minimum data capture for indicative measurements (%)	✓/✗	Required minimum time coverage for indicative measurements (%)	✓/✗
CO	Alphasense	90	✓	14	✓
	Winsen		✓		✓
NO_2	Alphasense	90	✓	14	✓
	Winsen		✓		✓
O_3	Alphasense	90 (summer Apr-Sept)	✓	10 (summer Apr-Sept)	✓
	Winsen		✗		✗
SO_2	Alphasense	90	✓	14	✓
	Winsen		✓		✓

Table S6: Number of hours on which measurements took place (N_{meas}) and number of valid hourly measurements in the measurement period (N_{valid}) from October 2019 to December 2020. The number of total number of hours for this specific period (N_{year}) was 10992 and for the case of O_3 (N_{summ}) was 4392.

		N_{meas}	N_{valid}
CO	**Alphasense**	6013	5028
	Winsen	4043	3338
NO_2	**Alphasense**	6013	3990
	Winsen	4043	3921
O_3 summer (Apr-Sept)	**Alphasense**	658	658
	Winsen	185	185
SO_2	**Alphasense**	6013	3864
	Winsen	4043	3904

Table S7: Estimated regression coefficients obtained via orthogonal regression between reference and LCS measurements.

		θ_0	θ_1
Alphasense	**CO**	255	0.27
	NO_2	12.5	0.56
Winsen	**CO**	358	0.12
	NO_2	22.6	0.44

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