

Article

Can Air Quality Gas Sensors Be Used for Emission Monitoring of Small-Scale Local Air Pollution Sources? Pilot Test Evaluation

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Abstract: In recent years we have seen a growing number of applications that use various sensory measurements of physicochemical features. Within the research project “Research on the identification of combustion of unsuitable fuels and systems of self-diagnostics of boilers combustion solid fuels for domestic heating”, the authors tested and evaluated the possible use of an air quality monitoring sensor unit for the measurement of operating parameters of solid fuel burning boilers and stoves. In the Czech Republic, programs to support citizens in the replacement of domestic boilers of poor combustion quality have been subsidized for several years. Unfortunately, no assessment of the impact of subsidies on air quality has been carried out. However, the increased pollutant emissions due to improper use of domestic boilers are supposed to be one of the greatest problems with domestic boilers. Hence, providing users with real-time feedback may lead to changes in combustion conditions and consequently to a reduction in air pollution. We focus on sensory measurements of CO, CO₂, NO, and VOCs as compounds that correspond to the operating conditions of the combustion process. The research included sampling, construction of the flue gas dilution duct, and the influence of direct measurement on the service life of the sensors.

Keywords: electrochemical sensors; photoionization sensors; air quality measurements; air pollution; local combustion; pollutant emissions



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1. Introduction

Air quality monitoring in recent years has undergone a great change: the introduction and promotion of sensory measurements. After approximately a decade of general use, there is positive feedback that results in even greater use and constant development, covering an ever wider range of monitored compounds and their concentration ranges. Sensory units can be deployed as sensor networks, densely covering areas and providing high spatial resolution. Contrary to traditional reference air quality measurement instruments that are bulky, expensive, and energy-demanding, sensor-based devices usually have low demand for power and are easy to install and relocate. Combined with the low cost, the mentioned features make sensory measurements possible almost anywhere. The availability and proliferation of sensor technology are closely connected with the issues of quality control and assurance (QC/QA) and suitability for the intended use.

The team of authors at VSB-TU Ostrava participated in two projects that used sensory measurements and sensor networks in air quality monitoring: “Intelligent system for identification of air pollution sources” (CZ.05.2.32/0.0/0.0/17_079/0006890) and “CLAIRO—Clean Air for Ostrava” (UIA03-123). For the projects, the database of results and visualization interface system Floreon was created and remains in use. Both projects showed the great potential of the technology and the necessity of careful checking of sensors, data transfers, and results in the database. The amount of data from sensor networks results in a need for an automated data validity check. Based on the experience obtained, the decision

was made to evaluate the feasibility of sensors' use in automatic control of combustion or combustion quality monitoring in small-scale boilers and heaters. According to the yearbooks of the Czech hydrometeorological institute, local combustion was responsible for 58.7% of the emission of particulate matter (PM₁₀) and even 98.2% of the emission of polycyclic aromatic hydrocarbons (PAHs) [1]. The government of the Czech Republic supports the ecologization of small-scale combustion in order to improve air quality through a partial grant for covering the purchase of newer and cleaner heaters and boilers. Apart from the quality of the boiler (emission class), the way of operation plays an important role in its overall emissions [2,3]. Therefore, the authors tried to explore the possibility of employing sensors in the field of long-term combustion exhaust monitoring. The aim was to outline the basic features of such a device using low-cost sensors (LCSs) that are the same as or similar to those used in ambient or indoor air quality monitoring. The employment of LCSs in air quality monitoring started the so-called citizen science-driven interest of laymen in air quality monitoring [4]. LCS-based instruments are available both as commercial products and do-it-yourself plans (overview presented in [4]). Thus, it remains to be seen whether an assumption can be drawn that if (at least some) boiler users obtained a low-cost exhaust quality tool, it may lead to increased awareness of exhaust quality, which subsequently could mean an improved control of the combustion process, more effective use of the heaters, and an improvement of air quality as a long-term goal.

2. Materials and Methods

2.1. Monitored Parameters

In the Czech Republic, the greatest burden for air quality is small-scale domestic heating, where wood, other biomass, and fossil fuels are burned either in old-style burners or sometimes new ones with the wrong method of usage. The legislation of the Czech Republic (Decree 415/2012 Sb. [5]) and the European Union (Commission Regulation 2015/1189 [6]) states the basic combustion-related pollutants to monitor:

- Carbon monoxide (CO);
- Sulfur dioxide (SO₂);
- Nitrogen oxides (NO_x—sum of NO + NO₂, presented as NO₂);
- Particulate matter (PM)—particles suspended in the exhaust fume;
- Organic compounds, presented as total organic carbon (TOC).

Another parameter needed in emission monitoring is oxygen or carbon dioxide, which shows the amount of excess air or flue gas dilution in the exhaust.

For all mentioned pollutants, an LCS alternative to professional measuring equipment is commercially available. Further, particle matter would not be a subject of testing, as PM measurement in fume ducts requires isokinetic sampling and short-distance collection on filters for gravimetric determination, which was not performed in our case. Moreover, optical particle counter-based sensors intended for air quality PM measurements are not suitable for measurement of the concentration range expected in combustion exhaust. In addition, the heated sampling probes contain particle filters to prevent clogging of the hoses.

2.2. Sensor Theory and Selection

Standard air quality sensors are intended to operate at ambient temperature and humidity, and the sensing parts are exposed to untreated indoor or outdoor air. The sensors for testing in combustion exhaust fumes were selected according to their usable concentration range. After initial research on commercial availability and specifications, it was obvious that none of the sensors would be itself able to measure native concentrations of pollutants in the exhaust duct, not to mention the conditions just downstream of the combustor. The concentrations of pollutants in the fumes are high, and they approach concentration values similar to those of ambient air after dilution.

Nowadays, sensors are manufactured in large quantities, and their lifetime is usually longer than 1 year (usual warranty for the end users). Unlike the reference instruments, the sensors are simple devices for a wide range of user-built installations, and their calibration

is not multi-point with rigorous robustness testing. They undergo a basic calibration during which the sensors are subjected to a pure analyte (calibration gas in most cases), and the output of each unit is adjusted to fit into voltage limits according to manufacturer specifications by the application of a calibration factor. Field tests focused on sensor response and cross-sensitivity have been conducted with respect to intended use [7–9], but recently, questions arose as to whether such field-calibrated sensors can be relocated [10,11]. Taking into account the behavior of the used sensors from long-term AQM [12,13], we checked the sensors for changes in behavior, and differences in measured concentrations of larger than 20% detected during routine checking compared to the previous measurement periods were considered as a sign of excessive wear and end of service lifetime; thus, such sensors discarded and replaced with new ones.

All used sensors were purchased from Alphasense, Ltd. (Braintree, UK), along with individual sensor boards (ISB)—manufacturer-developed low-noise circuit boards. Apart from the service life check described, all sensors were used as factory calibrated with no changes. The ISBs connect to an analog-to-digital (A/D) convertor and allow simple data collection by a control unit which was in our case a Raspberry Pi microcomputer running a script for multichannel data collection. The script starts upon system start and runs in a loop reading the raw voltage values from each ISB (sensor) and converting them into output values (ppm, ppb, %, $\mu\text{g}/\text{m}^3$, etc.) according to factory calibration.

2.2.1. Photoionization Detector (PID) Sensors

In photoionization detectors, the molecules are detected after ionization by high-energy UV radiation emitted from a gas discharge lamp (sensor and its parts are presented in Figure 1a, lamp specifications in Table 1). The sample in a gas phase diffuses into the chamber through a membrane that prevents interference caused by aerosols and dust. When exposed to UV radiation, molecules of ionization energy lower than that of the UV radiation are split into ions and electrons. In the electric field that is applied to the ionization chamber, charged particles migrate towards the respective electrodes and generate a current that is measured. The detection is unspecific as the generated current is proportional to the number of formed charged pairs, regardless of detected compounds. According to manufacturers, the expected lifetime of the sensor body is 5 years; UV lamps and ionization chambers are considered consumables with an expected operating time of 5000 h or 24 months [14]. Commonly used lamps provide energies below and around 10 eV; specific values depend on gas filling and spectral characteristics of the used window material (Table 1). While 11.7 eV variants of lamps exist, they are not suitable for long-term operation as their operating time is very limited. There are two reasons for such a short lifetime: The first is the degradation of the window material, lithium fluoride, which is degraded by moisture absorption. The second reason is a process of solarization, a deposition on the window surface induced by incident UV radiation leading to window tinting. Therefore, the limits of the 11.7 eV lamps reduce the service life of the sensors to about a month of intermittent operation or up to 25 h of continuous operation [15–17].

Table 1. Mini-PID sensor specifications (manufacturer’s technical information [18,19]).

| Sensor Marking | Filling Gas | Ionization Energy (eV) | Measurement Range (ppm Isobutylene) |
|----------------|----------------------|------------------------|-------------------------------------|
| PID-H9 | Xenon | 9.6 | 0–8000 |
| PID-HX | Krypton ¹ | 10.0 | 0–100 |
| PID-AH | Krypton | 10.6 | 0–40 |

¹ According to the manufacturer, the 10.0 eV sensor contains the same Kr lamp as the 10.6 eV sensor and an extra filter restricting radiation energy to 10.0 eV.

PID sensors are most commonly used for the detection of volatile organic compounds (VOCs), but due to the nonspecificity of detection, they do not allow for traditional calibration. The variants of PID sensors are listed in Table 1.

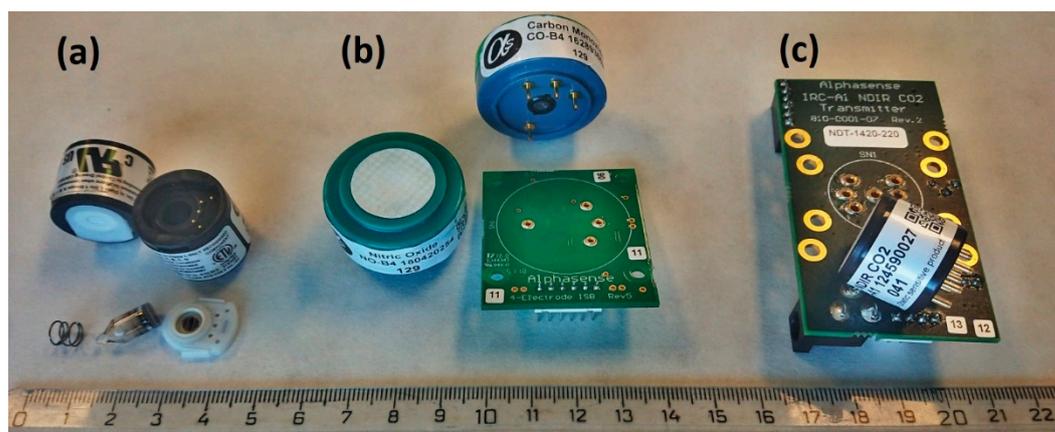


Figure 1. The used Alphasense sensors with dimension scale. (a) Assembled PID sensor and its components (sensor body, gas discharge lamp, and ionization chamber with electrode stack). The outer diameter of the sensor is 20 mm. (b) B4-series electrochemical sensors and the corresponding sensor board (ISB). The outer diameter of the sensor body is 32 mm, height 16.5 mm. (c) IRC-A1 CO₂ sensor with corresponding circuit board that houses independent power supply.

2.2.2. Electrochemical Sensors: Alphasense B4 Series

Generally, electrochemical sensors detect gases that diffuse from the near surroundings through a gas-permeable membrane preventing droplets from entrance and interaction. Inside the sensor cell, an electric field is applied to the electrolyte, forcing electric charge migration between the working electrode and counter-electrode where the electron exchange reactions (oxidation and reduction) occur and a change in the current is detected [20–22]. The selectivity of the sensor is tuned by electrolyte composition, polarity, and intensity of the electric field that together influence the sensing of analytes.

The used Alphasense B4 series sensors (Figure 1b) use an advantageous 4-electrode arrangement employing an auxiliary electrode for better resolution. Technical specifications of NO-B4 and CO-B4 sensors [23,24] are presented in Table 2.

Table 2. Technical specification of the Alphasense B4 series sensors for detection of NO and CO.

| Sensed moiety | NO | CO |
|--------------------|---|---|
| Limit of detection | 20 ppb | 4 ppb |
| Measurement range | 0–20 ppm | 0–500 ppm |
| Sensitivity | 1 ppb | 25 ppb |
| Uncertainty | <30% | <30% |
| Interference | H ₂ S, NO ₂ , Cl ₂ , SO ₂ | H ₂ S, NO ₂ , Cl ₂ , SO ₂ |

2.2.3. Carbon dioxide sensor CO₂-IRC-A1

The detecting principle of the used sensor Alphasense CO₂-IRC-A1 is based on the non-dispersive infrared (NDIR) absorption of gases. Infrared radiation at specific wavelengths (called the absorption band) is absorbed by the analyzed gas in the measurement chamber. The source of infrared light radiates through a filter that allows the passage of only the wavelengths specific to the gas of interest. When the analyzed gas is present in the measurement chamber, part of the passing radiation is absorbed before reaching the detector. The presence and concentration of target gas (in our case, CO₂) influence the decrease in transmitted radiation. The reference signal is measured at different wavelengths, unaffected by the presence of the detected gas. Using results from both measurements, the sensor can compensate for differences in radiation intensity commonly associated with the aging of light sources. For necessary temperature correction, the sensor is equipped with an internal thermistor. The sensor unit was used with a manufacturer-supplied circuit board (Figure 1c). Technical specifications of the IRC-A1 CO₂ sensor can be seen in Table 3.

Table 3. Technical specification of the Alphasense NDIR CO₂ sensor—model IRC-A1.

| | |
|-----------------------|-----------------|
| Target substance | CO ₂ |
| Measurement range | 0–20% |
| Humidity range | 0–95% |
| Zero resolution | 1 ppm |
| Full-scale resolution | 500 ppm |

2.3. Sampling and Dilution Route

The sampling route is a system of distribution and dilution components leading a representative part of the exhaust fumes to the measurement device. The fumes were sampled directly in the duct using a heated probe PSP 4000 (M&C Tech Group, Rattigen, Germany). A stainless tube of 6 mm inner diameter was secured in a threaded fitting fixed in the wall of the duct. In the heated body of the probe, the particulate matter is filtered by the 2 µm ceramic filter, and the gases are transported by a heated hose (180 °C, Winkler AG, Heidelberg, Germany) to the cascade of ejector dilutors (VKL 10 E and VKL 10 dilutors, Palas GmbH, Karlsruhe, Germany, Figure 2).

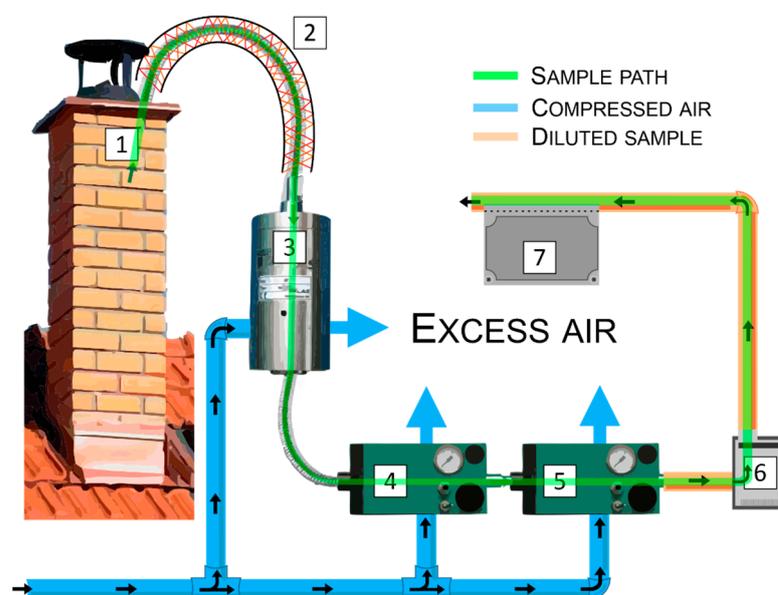


Figure 2. Schematic illustration of the measurement setup: (1) exhaust; (2) heated duct of sampled exhaust fumes; (3) VKL 10 E dilutor; (4,5) VKL 10 dilutors; (6) membrane pump; (7) sensor measuring device.

Each of the dilutors is capable of dilution of the inlet gas in a 1:10 ratio (according to the manufacturer-supplied hydrodynamic calibration certificate), and they are physically stackable, so that the output jet of the first dilutor acts as an input jet of the next one. Thus, the final dilution factor of 100 is obtained for two stacked dilutors, and the final dilution factor of 1000 is obtained in the case of three stacked dilutors. Regardless of the final dilution ratio, the diluted output gas must be actively transferred from the dilutor outlet into the measurement device. For the transfer, a commercially available membrane pump (constant flow rate 2.5 L/min) was installed on the transfer line. All used tubing was made of polytetrafluoroethylene (PTFE).

2.4. Reference Methods for Experimental Monitoring

The combustion testing was performed in the testing laboratory of the Energy Research Centre (ERC) at the VSB-TU Ostrava, which is a Notified Body under the EU Council regulation No. 305/11. The sensory unit was used for parallel monitoring of combustion testing of a small-scale manually fed domestic heating burner using wooden logs in

2 combustion modes. In the first run, the combustion was performed at stoichiometric conditions, and in the second run, the air intake was reduced and the combustion process was expected to produce greater amounts of CO and organic products in the flue gas [25]. The flue gas was measured initially using all 3 dilutors at a dilution factor of 1000 and gradually excluding one dilution step at a time, leaving the parallel measurement period for comparison of at least 10 min. All recorded sensory data were compared to results obtained by parallel measurements using reference flue gas analyzers ABB EL3020 (determination of CO, CO₂, NO, O₂, SO₂ by infrared spectrophotometry) and ABB AO2020 (determination of total organic carbon as propane equivalent with flame ionization detector (FID), both ABB, Frankfurt, Germany). The reference analyzer always measured undiluted flue gas throughout the whole combustion process (several hours in a row).

2.5. Statistics

All statistical calculations were conducted with the StatPlus 6.1.1 software (AnalystSoft, Inc., Walnut, CA, USA). The presented correlation coefficients were calculated as Pearson correlation coefficients.

Validation factors were determined from long-term averages as a coefficient applied to sensor results to match with reference measurement results over the same time period. Scatter plots were used for the visualization of the variable pairs. Reference method results were considered independent values, and sensory results were considered dependent variables for the comparisons. The scatter plots contain regression equations describing relations between explanatory variables (reference measurement dataset) and response variables (LCS measurement dataset), confidence intervals (CIs), and prediction intervals (PIs) based on the linear regression of both datasets, at a 95% confidence level.

3. Results

3.1. Sample Transport and Dilution

Although the ejector dilutors are supplied with a calibration certificate, the figures were obtained by hydrodynamic calibration. The actual dilution for gaseous samples was checked by diluting reference methane gas (19.95% *v/v* in nitrogen, SIAD, Bergamo, Italy) and analyzing the diluted product using a gas chromatograph with a flame ionization detector (Agilent 7890, Agilent, Santa Clara, CA, USA).

There are two drawbacks to the chosen experiment arrangement regarding the location of the membrane pump between the dilutors and measurement apparatus. First, the outcome of the dilutors must be actively pumped out of the last unit in cascade; otherwise, the whole sample-air mixture escapes with the excess air stream. Second, the sensor unit was designed to mainly operate in ambient air (emission monitoring), so it could not be effectively sealed. Thus, the dilution ratio check was performed with the membrane pump located downstream of the diluter cascade. To avoid overpressure at the input, a 25-L Tedlar sampling bag was filled with the reference gas to be drawn by the first diluter. The diluted gas was pumped by the membrane pump into a 10-L Tedlar sampling bag and analyzed. All dilution measurements were performed in triplicate. The results are presented in Table 4.

Table 4. Dilution of the 19.95% *v/v* reference methane gas.

| Dilutors | Output Concentration | Dilution Factor |
|-----------------------|----------------------|-----------------|
| 1: VKL 10E | 2.09% | 9.5 |
| 2: VKL 10E + VKL 10 | 0.25% | 81.2 |
| 3: VKL 10E + 2xVKL 10 | 0.026% | 774 |

The figures are close to theoretical factors in the cascade, so dilution marking of the diluter cascade could be used in theoretical figures (10×, 100×, and 1000×). Results are acceptable, provided that sensory measurements are indicative by definition and the

dilution for the measurements indoors or near the living area probably would have to use a different setup omitting ejector diluters and a source of compressed air.

3.2. CO Sensors

The experiment was performed according to the procedure in Section 2.3. The measurements were performed with undiluted flue gas and with consecutive dilutions of 10 \times , 100 \times , and 1000 \times . The purpose of this experiment was to evaluate the correlation of sensory CO measurement to the reference CO analyzer at variable dilution ratios.

During the experiment, the flue gas was successively diluted 1000 \times , 100 \times , 10 \times , and 0 \times . The graph in Figure 3 shows the correlation between the sensory and reference instrument measurements; Figure 4 presents the regression of the obtained datasets. The measured data are in agreement, with distinctly observable peaks. The Pearson's correlation coefficient calculated for individual dilutions were 0.94, 0.96, 0.79, and 0.77, respectively (result summary in Table 5). The Pearson's correlation coefficient calculated for the whole dataset throughout the experiment was 0.91.

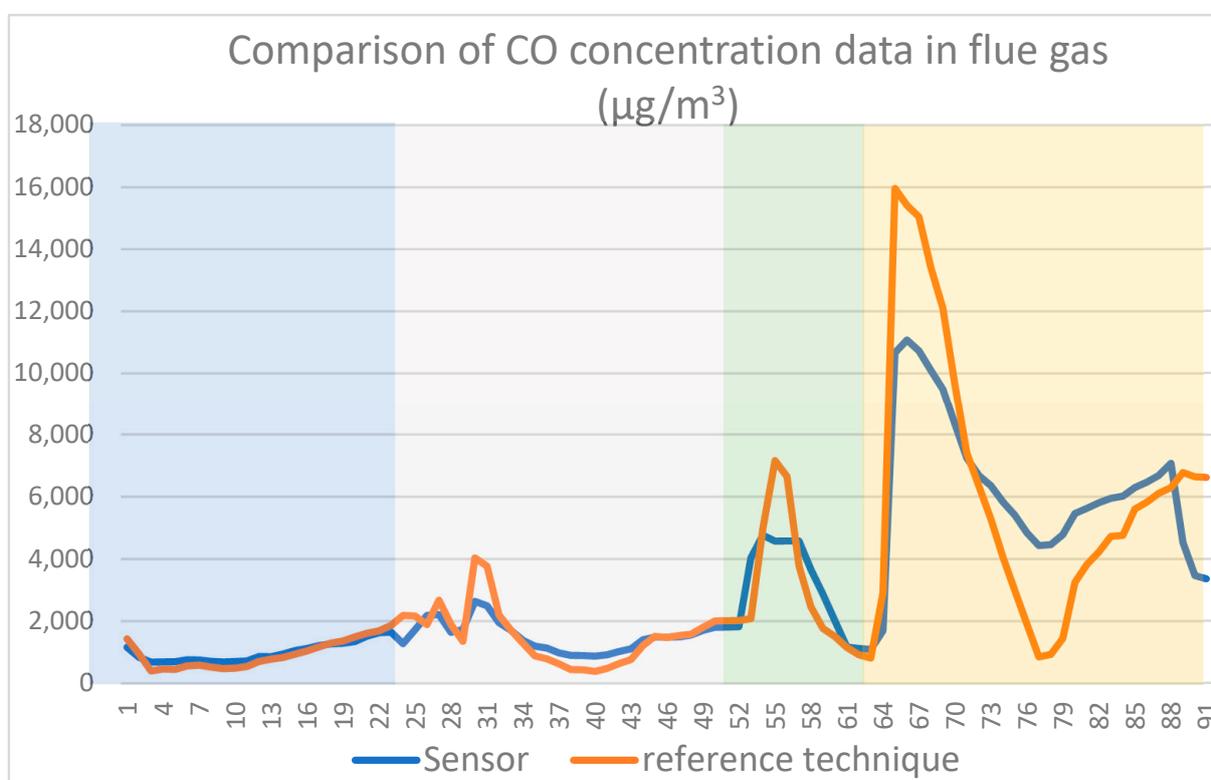


Figure 3. Measured CO data—paired measurements for individual dilutions. The individual colors correspond to dilutions of 1000 \times , 100 \times , 10 \times , and 0 \times (left to right).

In general, we can conclude that sensory and reference measurements correlate well. The best results were obtained at 100 \times dilution with sensors following the reference measurement trend but decreasing in responsivity when measuring less diluted sample gas. A lower dilution could easily lead to saturation and, under extreme conditions, to sensor damage and associated signal degradation. Another issue can be observed with higher concentrations, where the measurement dynamics decreases. Both issues can be addressed with the proper dilution of the sampled gas. However, it should be noted that the higher the dilution, the lower the difference between the information-bearing signal component and signal noise. As the noise component gains importance, the meaningfulness of data may be significantly impaired.

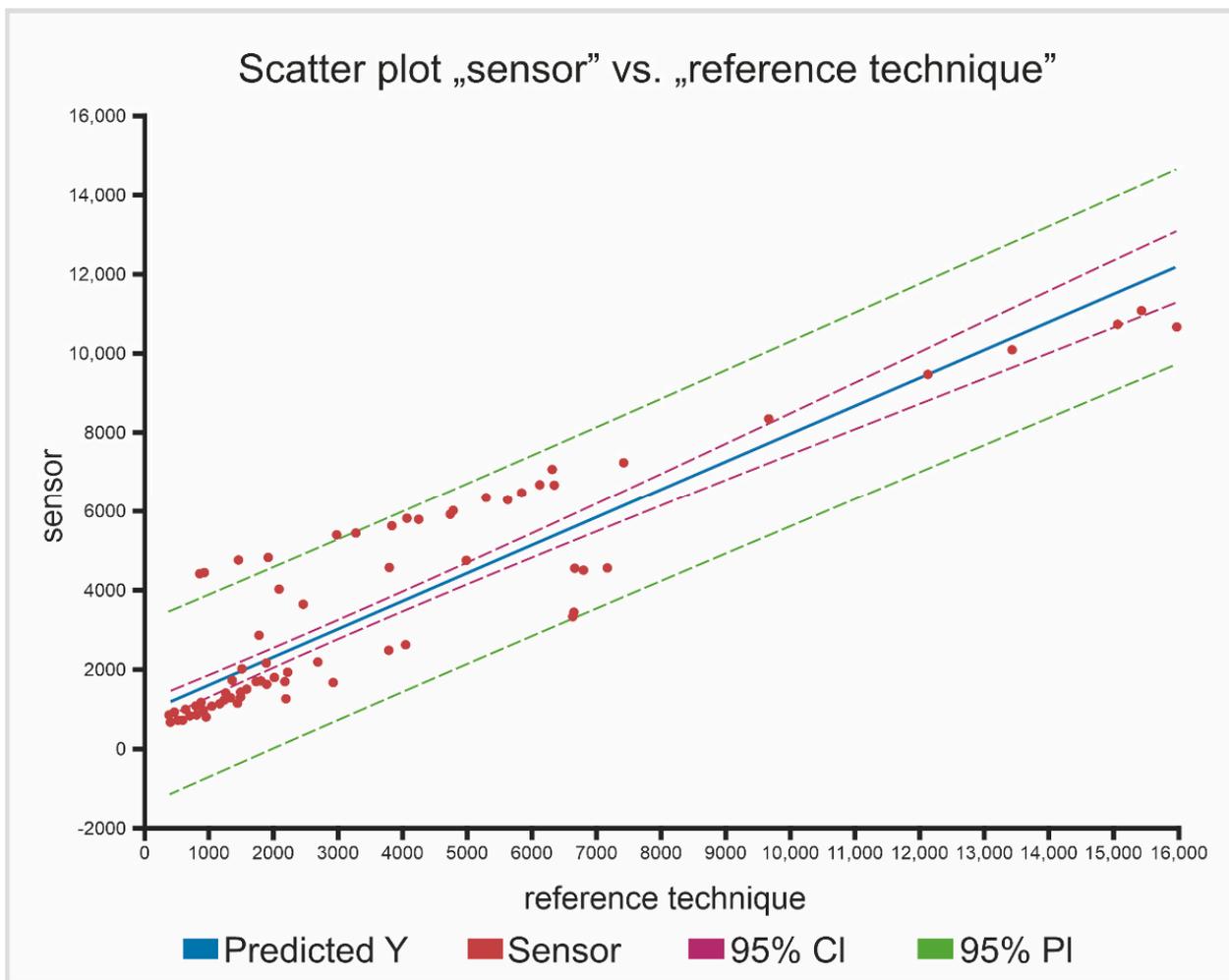


Figure 4. Regression relation between concentrations determined by reference method and CO sensors ($\mu\text{g}/\text{m}^3$). $\text{Sensor} = 904.32 + 0.71 \times \text{reference analyzer}$. The regression of the CO sensor and the reference method confirms significant agreement over a large concentration range. CI = confidence interval, PI = prediction interval.

Table 5. Basic statistic description of measurements with CO sensors and the reference analyzer.

| Statistical Parameter | CO Sensor | Reference Analyzer |
|-----------------------|-----------------------------------|-----------------------------------|
| Arithmetic mean | 3088.2 $\mu\text{g}/\text{m}^3$ | 3089.0 $\mu\text{g}/\text{m}^3$ |
| Minimum | 684.8 $\mu\text{g}/\text{m}^3$ | 386.1 $\mu\text{g}/\text{m}^3$ |
| Maximum | 11,074.9 $\mu\text{g}/\text{m}^3$ | 15,595.6 $\mu\text{g}/\text{m}^3$ |
| Median | 1707.1 $\mu\text{g}/\text{m}^3$ | 1708.7 $\mu\text{g}/\text{m}^3$ |
| Geometric mean | 2184.2 | 1905.6 $\mu\text{g}/\text{m}^3$ |
| Pearson | | 0.91 |

From the available data, we can assume that the Alphasense CO-B4 sensor could be applicable for the measurement of flue gases under certain conditions and scenarios, regardless of dilution. The only concern would be exceeding upper measurement and overgas limits that can occur when the combustor is running on a low oxygen level and high amounts of organic compounds and CO are produced (illustration given in Figure 5). In such cases, the measured concentrations can reach values as high as 10-fold the values measured at stoichiometric conditions.

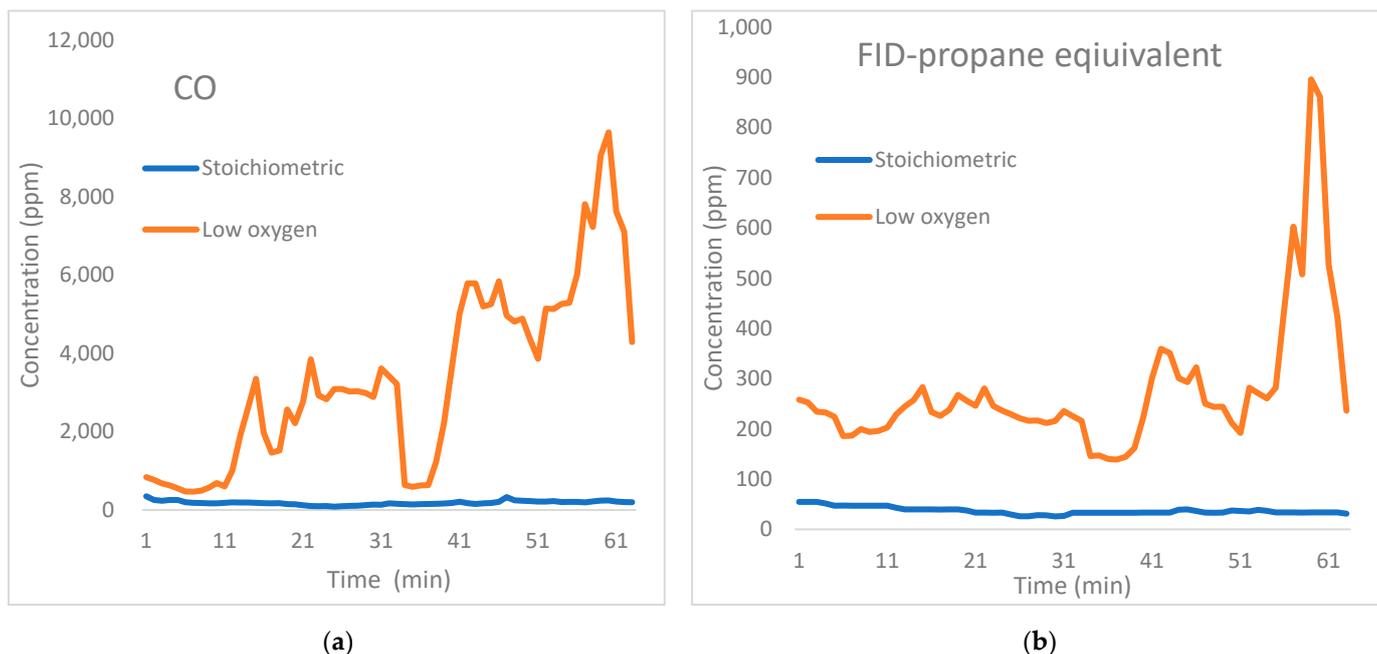


Figure 5. Comparison of concentration of combustion process products at stoichiometric conditions and low oxygen intake for CO (a) and organic compounds analyzed by FID (b).

3.3. NO Sensors

The experiment was performed according to the procedure mentioned in Section 2.4. The examined dilutions were successively 1000×, 100×, 10×, and 0×. The purpose of this experiment was to see how the sensory measurement correlates with the reference analyzer measurement at different dilution ratios. The measurement proceeded from the highest dilution (1000×) to non-diluted flue gas. The measurement results can be seen in Figure 6 and Table 6.

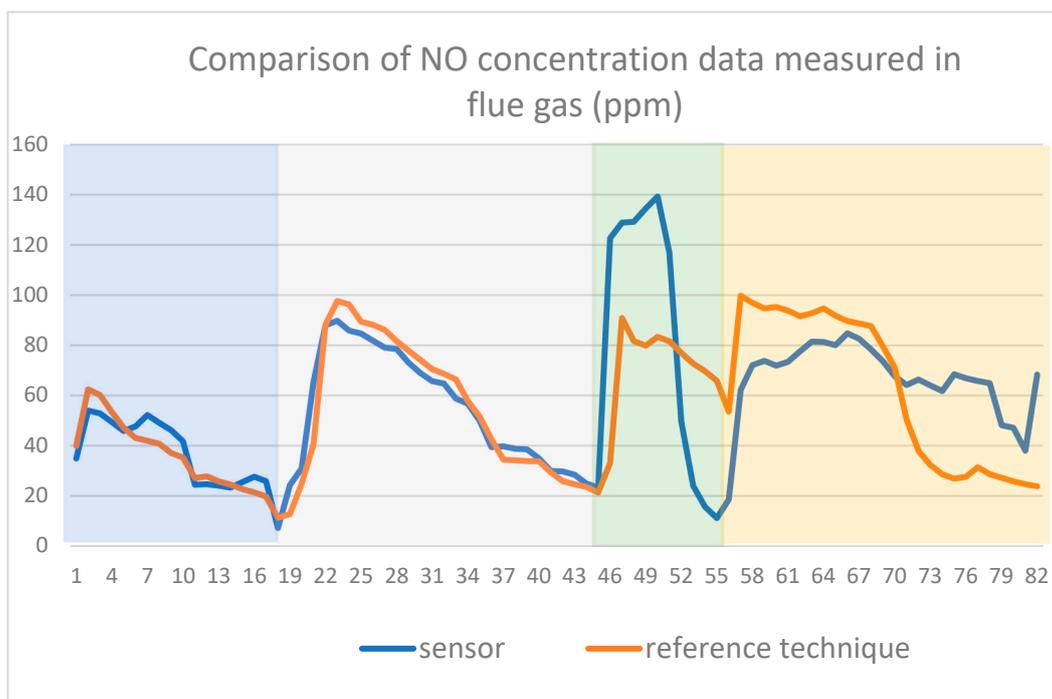


Figure 6. Measured NO data—paired measurements for individual dilutions. The individual colors correspond to dilutions of 1000×, 100×, 10×, and 0× (left to right).

Table 6. Basic statistic description of measurements with NO sensors and the reference analyzer.

| Statistical Parameter | NO Sensor | Reference Analyzer |
|-----------------------|-----------|--------------------|
| Arithmetic mean | 58.6 ppm | 55.4 ppm |
| Minimum | 7.2 ppm | 11.3 ppm |
| Maximum | 139.3 ppm | 99.8 ppm |
| Median | 60.3 ppm | 50.9 ppm |
| Geometric mean | 50.93 ppm | 48.0 ppm |
| Pearson | | 0.64 |

The signals of both devices correlate well at higher dilutions (1000×, 100×) in sensory measurement. The respective Pearson’s correlation coefficients calculated for individual dilutions are 0.91, 0.97, 0.3, and 0.71 (left-to-right). The Pearson’s correlation coefficient of the entire dataset corresponds to 0.64. The relation between the sensor and reference analyzer can be seen in Figure 7. It can be concluded that the best choice for measurement would be the 100-fold dilution. This dilution shows the highest level of agreement with the reference method similar to that of the CO sensor.

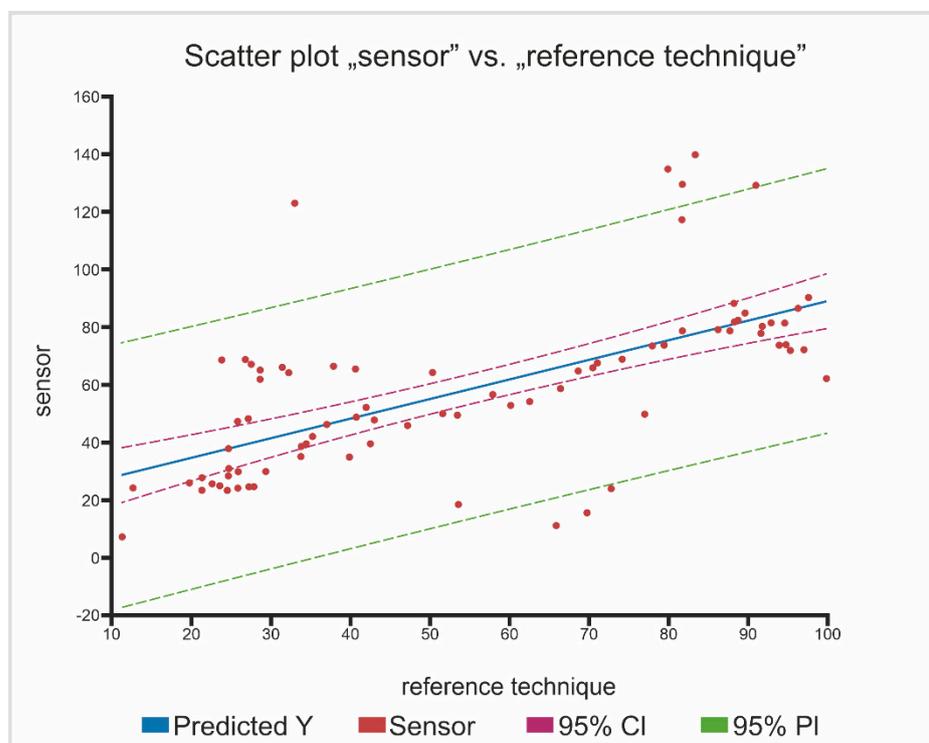


Figure 7. Regression relation between the reference method and NO sensors (ppm). $\text{Sensor} = 21.05 + 0.68 \times \text{reference analyzer}$. The regression of the CO sensor and the reference method confirms medium-level agreement.

The box plots in Figure 8 show the ideal distribution of measured concentrations for the reference method and a slight shift toward higher values for the NO sensory measurement.

In Figure 7, scattered points show significant differences in Pearson’s correlation coefficients for individual dilutions. If the influential points are removed (datasets presented in Figure 6 from point 46 onwards), the Pearson’s correlation coefficient significantly improves from 0.64 to 0.97. Therefore, at higher dilution (factors 1000× and 100×), the correlation of NO sensors and reference method can be assessed as very good. The behavior of NO sensors in emission measurements resembles the behavior of NO₂ sensors in emission measurement: the individual concentration values are dispersed, but the averaged values are usable [4]. The Alphasense NO-B4 sensor could be applicable for flue gas measurement. However, dilutions of 100× or higher should be considered in such applications.

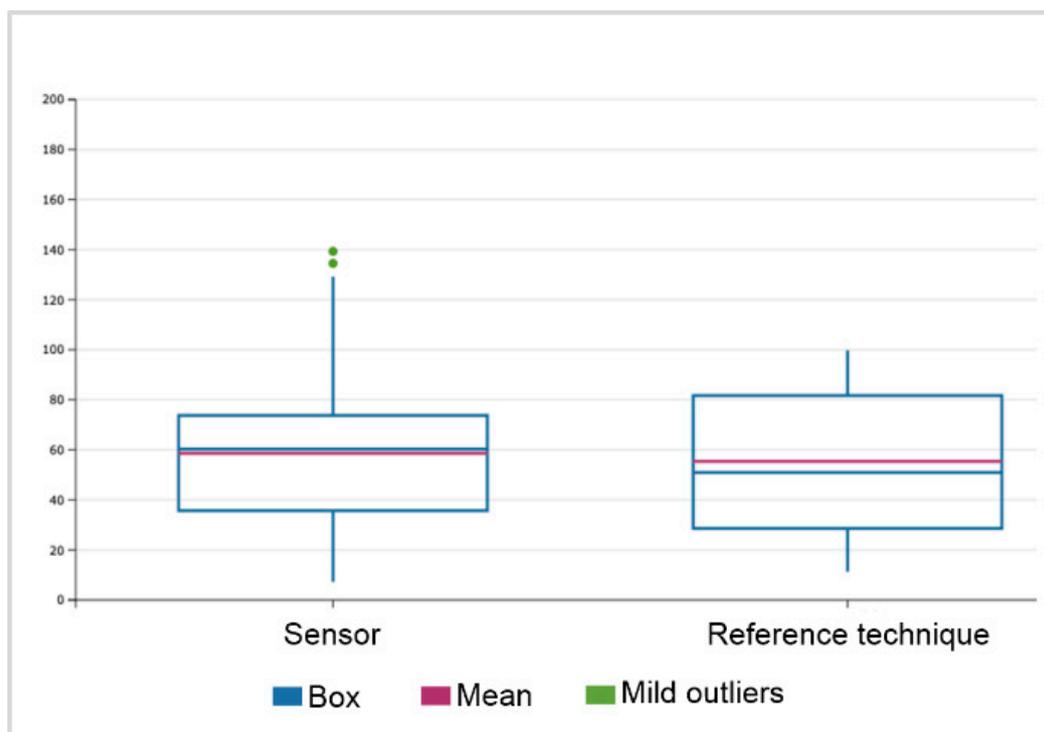


Figure 8. Box plots of the entire dataset of acquired NO measurements.

3.4. CO₂ Sensors

The CO₂ sensor pre-set parameters were checked by measuring standard gas containing a certified amount of CO₂ (SIAD, Braňany, Czech Republic). Before the measurements, zero signal in pure nitrogen gas (SIAD, Braňany, Czech Republic) was recorded. Output voltage values for zero and 10% certified CO₂ gas were assigned as correction factors for the A/D signal conversion. Zero readings of the sensor were $0.009 \pm 0.01\%$ (v/v), and the certified 10% value measured with manufacturer preset values was $8.88 \pm 0.03\%$ (v/v); after correction, the measured value was $10.0 \pm 0.03\%$ (v/v).

As the used sensor is intended for the measurement of CO₂ concentration in native (undiluted) flue gas, it covers concentrations from 0 to 20%; therefore, dilutions of 100× and 10× were tested. In the case of 100× dilution, the sensor did not react to the present concentration and provided only zero value readings.

In periods of measurement in native flue gas, the sensor measured in accordance with the analyzer; results are presented in Table 7 and Figure 9.

Table 7. Overview of measurements with CO₂ sensors and the reference analyzer.

| Measurement | Sensor (% v/v) | Reference Analyzer (% v/v) | R | Duration (min) |
|---------------------------|----------------|----------------------------|------|----------------|
| Flue gas undiluted (S*) | 13.99 | 13.93 | 0.32 | 30 |
| Flue gas diluted 10× (S*) | 0.36 | 13.16 | 0.76 | 22 |
| Flue gas undiluted (LO) | 14.07 | 14.68 | 0.88 | 26 |
| Flue gas diluted 10× (LO) | 0.34 | 12.05 | 0.47 | 120 |

S* = stoichiometric combustion; LO = low oxygen combustion.

The differences in Pearson’s correlation coefficients correspond to the measurement arrangements. In the optimal case, the sensor data should correlate tightly with analyzer data; the decreased correlation values indicate instrumental problems, in our instance mostly condensation in the parts of the duct where the wet gas cooled, out of visual control.

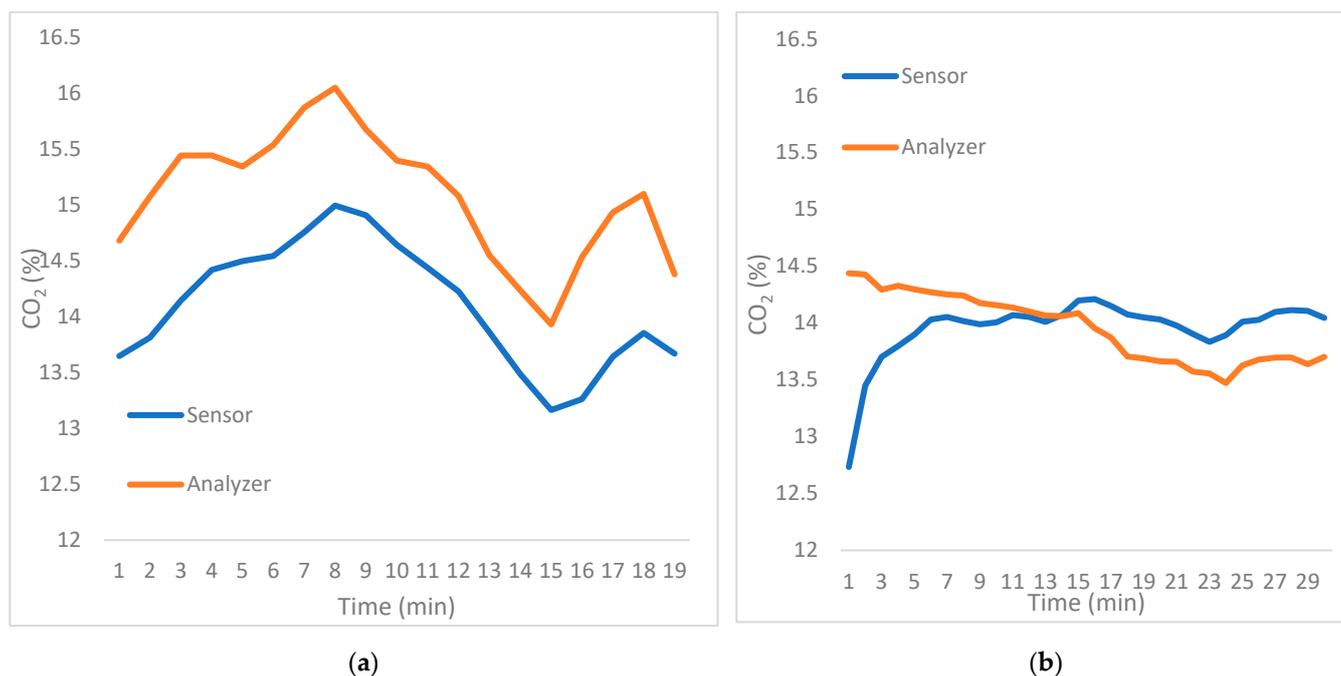


Figure 9. Comparison of 2 native flue gas measurements: (a) good correlation ($R = 0.88$), curves reflect the trend; (b) poor correlation ($R = 0.32$), curves intersecting, indication of a possible problem in the duct to the sensor unit.

3.5. PID Sensors

Photoionization detector sensors were chosen after they proved suitable for VOC monitoring in ambient air [13]. Due to their working principle, they were considered a better option than electrochemical and semiconductor-based VOC sensors as those can undergo a reduction in service lifetime when exposed to condensing humidity contained in the sample [22], which was anticipated. According to the conclusions of our previous work, the usability of the PIDAH9 sensor of 9.6 eV ionization energy was evaluated in an environment containing higher concentrations of VOCs than those in ambient air.

For the calibration, all three varieties of PID sensors were exposed to compounds in a gaseous form prepared in the laboratory and analyzed by gas chromatography; a detailed description is given in our previous work [13]. We also concluded that in mixtures of compounds, the responses of the sensors are additive but highly inconclusive and incalculable; the best way to estimate the concentration was a simple linear regression of signals derived from benzene concentrations. Adding to the downside of PIDs, it has to be stated that the presence of methane and other gas molecules containing up to three carbons causes the “quenching” of the signal by UV absorption of the UV radiation without ionization. In Table 8, the responses of the PID types to benzene are presented.

Table 8. Responses towards analyzed gasses. Concentrations were determined by gas chromatography.

| Benzene (%) | PIDHX (mV) | PIDAH (mV) | PIDAH9 (mV) |
|-------------|------------|------------|-------------|
| 0.000 | 40.00 | 47.00 | 36.00 |
| 6.440 E-04 | 44.50 | 58.70 | 35.80 |
| 9.390 E-04 | 103.80 | 252.70 | 37.10 |
| 0.016 | 923.50 | 2374.00 | 53.80 |
| 0.100 | 2398.00 | 2373.00 | 160.00 |
| 0.961 | 2397.00 | 2373.00 | 954.00 |

In Table 9, the correlations of sensor responses to VOC mixtures are presented. As the number of variables used increased, the degree of noise increased and the correlation decreased.

Table 9. Correlations of PID responses to VOC concentrations in verification mixtures.

| PIDHX vs. | R ² |
|-----------------------------|----------------|
| Benzene (B) | 0.85 |
| Benzene + Toluene (T) | 0.61 |
| B + T + Ethylbenzene (E) | 0.39 |
| B + T + E + Xylene (X) | 0.31 |
| B + T + E + X + Styrene (S) | 0.29 |

After the measurement, we found that the sensor response towards the native flue gas is very weak. After recalculation of the data with the validation factor, we found that a similar trend is clearly visible (Figure 10). Splitting the data into three segments corresponding to applied dilutions (1000×, 100×, and 10×, left-to-right) and comparing individual sensor types with the reference method, we found that the Pearson’s correlation coefficient was 0.92 for 1000× dilution for HX and AH sensors. In the segment with 100× dilution, the Pearson’s correlation coefficient was lower, 0.81 and 0.79 for AH and HX types, respectively, and further decreased when the more concentrated samples were measured. Statistics of the whole dataset are presented in Table 10.

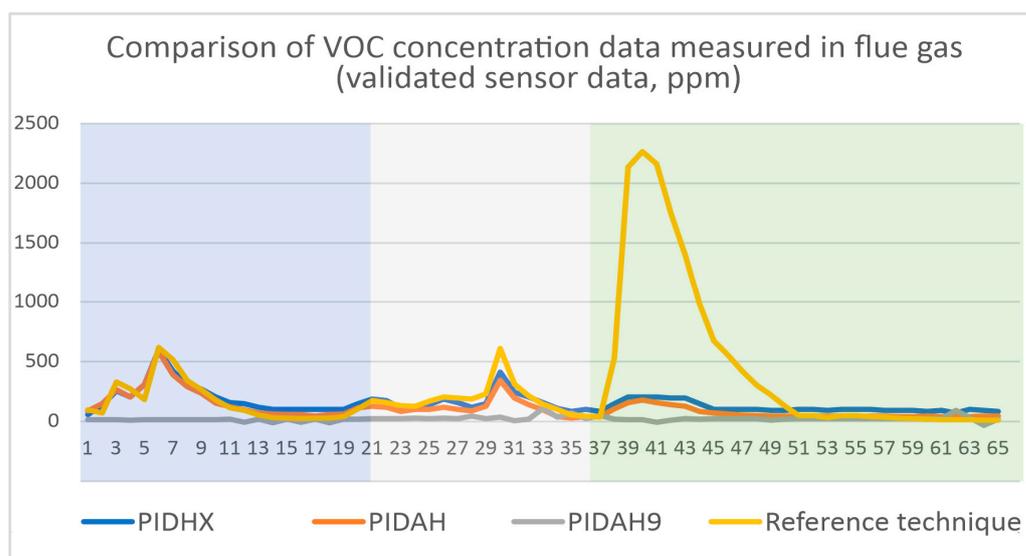


Figure 10. VOC sensor measurement profiles compared to the reference technique. Dilutions are 1000×, 100×, and 10× (left to right).

Table 10. Basic statistical description of measurements with PID sensors and the reference analyzer.

| Statistical Parameter | PIDHX (ppm) | PIDAH (ppm) | PIDAH9 (ppm) | Reference Analyzer (ppm) |
|-----------------------|-------------|-------------|--------------|--------------------------|
| Arithmetic mean | 149.3 | 236.1 | 25.9 | 245.2 |
| Median | 117.3 | 96.7 | 22.2 | 54.6 |
| Pearson | 0.32 | 0.09 | 0.16 | - |

Measured concentrations are very low, resembling air quality monitoring [1]. As shown in Figure 11, all displayed dependencies point towards a poor level of tightness between the sensors and the reference technique.

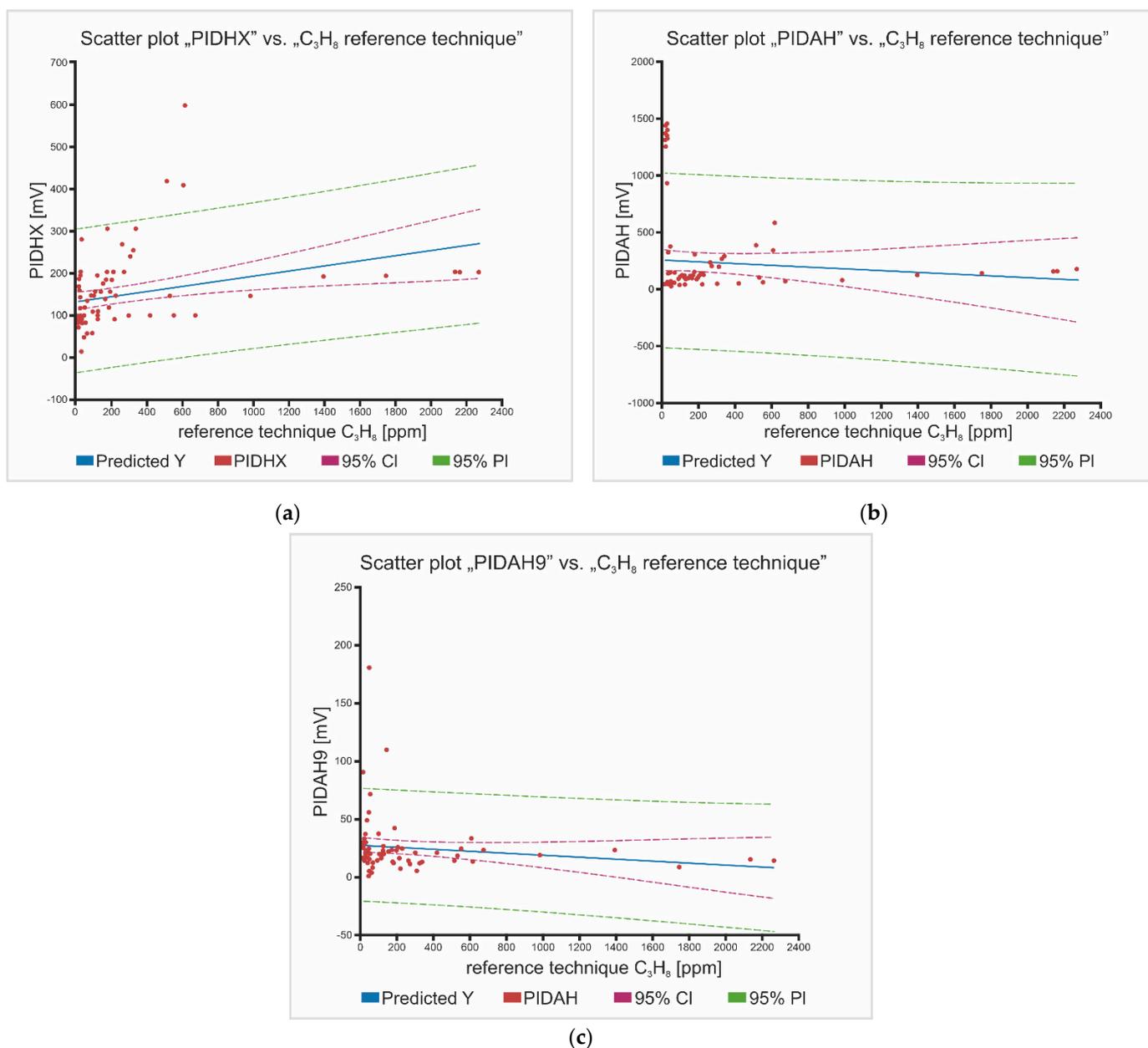


Figure 11. Regression figures of the relationship between the sensors and the reference method. Displayed are PIDHX (a), PIDAH (b), and PIDAH9 (c) sensors.

4. Discussion

The experiment was purposely conducted with manually stoked wood-firing combusters as they usually are not equipped with any regulation systems. Contrary to them, automatic-fed combusters use rather homogeneous fuel and at least some regulation of the feeding. Manual stoking of wooden logs leads to different stages of the combustion process that occur both regularly in the stoking cycles and irregularly along the combustion; e.g., when ends of wood logs lean against one another while the middle parts become adjacent after burning the close parts, temperature decreases and the fire starts producing carbon monoxide and various organic compounds [25] even in the stoichiometric combustion setting. These episodes can be identified in the measurement record (spikes of concentration), and the irregularities can be corrected. A comparison of CO and organic compound concentration developments under both conditions is presented in Figure 5. To our knowledge, the field of sensing mostly inorganic gases by means of semiconductor-based sensors is

rapidly growing. Fine-tuning of sensor properties either by composition [26] or structure of various materials (e.g., carbon nanotubes [27]) shows promise for the further development and use of sensors.

The authors are aware that currently there are available instruments on the market that are based on sensor technology and have probes that can be placed directly into the flue gas flux. However, to our knowledge and to the extent of information accessible to the general public, they are intended for professionals (e.g., Testo 350, used for testing by certified personnel). Moreover, instruments of the mentioned kind are based on metal-oxide (semiconductor) sensors that require dry gas for measurement (and hence some kind of water trap) as condensing vapor destroys the sensors. Such instruments are neither suitable nor intended for long-time measurements. Drawbacks to the use of semiconductor sensor instruments are listed in the user manual [28]:

1. Must not be used for continuous measurements (p11);
2. Battery operation time circa 5 h (or 2.5 h, if gas cooler and IR module are on; p20);
3. Measurements with pressure sensor must not be longer than 5 min (pp74/75).

In the field of air quality monitoring, the measured concentrations of pollutants in ambient air are considered the final dilution step of all pollutants released from various sources into large air volume in an area widely surrounding the sources at local meteorological conditions. Contrary to that, reference measurement of emitted pollutants in the exhaust fumes bound to a particular source requires simultaneous monitoring of CO₂/O₂ concentration needed for comparison of the combustion devices at standard conditions. The first of the most important questions raised is whether oxygen or carbon dioxide needs to be monitored to allow the calculation of standard conditions as required for combustor emission testing. The second question aims at the sampling and dilution issue: The flue gas measurement cannot be conducted by passive measurement like the AQM. Hence, sampling and dilution would have to be technically dealt with as well. A solution to this issue should avoid the need for a large amount of compressed air and use low-cost components.

As shown in Figure 11 and Table 10, the PID-AH9 sensor is almost inactive during the measurement, contrary to the anticipation that it would respond to higher concentrations of hydrocarbons at low dilution. This may be due to the composition of analyzed flue gas in which, compared to higher energies, the lowest UV radiation energy of 9.6 eV is more susceptible to quenching in a non-uniform environment of many interfering substances. It is known that in presence of substances capable of absorbing UV radiation without ionization, the PID signal is significantly reduced. For example, methane of concentration 2.5% by volume can quench the signal by 50% [29,30] due to the fact that methane has strong absorption in the region of the PID's lamp energies [31].

5. Conclusions

The results show a need for dilution for most of the monitored parameters. In conducted experiment, flue gas was diluted with dry pressurized air that prevents condensation in the duct and interference of the condensate with flue gas. CO, NO, and PID sensors could be used at a unified dilution of 100×. For better results of organic compounds, further dilution to 1000× for the PID sensors would be appropriate. In this case, a CO₂ sensor of a lower measurement range would be more suitable.

Taking into account that the presented results in the section on measurements conducted with low-cost sensors used in the experiment were obtained with professional diluters designed for the task, in particular, the PID sensors are currently unsuitable for emission measurements. It can be assumed that, without large dilution, the signal would be quenched by compounds undetectable by PID. It has to be emphasized that the group of compounds detectable by PID sensors differs from the larger group detectable by FID.

A possible solution could be to pre-treat the sample prior to measurement. However, such treatment would be challenging, and currently almost impossible for the intended application—on-site monitoring directly on chimneys as local pollution sources. Therefore,

the advantage of tested sensors in ambient air monitoring, namely the development of concentration in space and time, is neglected in terms of analysis of air-polluting compounds at the source. Rapid indicative measurement of flue gas may be possible in the scale of citizen science for the laymen who become interested and educate themselves, but certainly not (yet?) in relation to automated combustion process control. Other options will have to be sought—possibly electrochemical, or other sensor types, maybe adding a methane sensor and further calibration of sensor clusters by advanced computing methods.

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