Performance Evaluation of Low-Cost BTEX Sensors and Devices within the EURAMET Key-VOCs Project †

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Abstract: The KEY-VOCs project is a EURAMET joint research project focused on key Volatile Organic Compounds (VOCs) in air. One of its activities is the evaluation of sensors-based measurement systems. In Europe, the monitoring of benzene in ambient air is mandatory as set by the European Directive for air quality (AQD) [1]. This Directive states that the reference method of measurement shall consist of active or on-line sampling followed by gas chromatography [2]. These methods are time consuming, expensive to implement and not easily portable prohibiting more local estimation of the population exposure. However, the AQD allows using indicative measurements with higher uncertainty than those of the reference methods. Sensor systems are good candidates for indicative methods with the additional ability of near-to real-time measurements.

Keywords: PID based sensors; semiconductor and amperometric sensor; mini GC; portable on-line measuring devices; benzene; volatile organic compounds

1. Introduction

Low-cost sensors are attracting more and more interest, as they would be able to provide a cheaper way to monitor air quality on a larger scale. However, if the current sensor technology can be considered efficient enough for inorganic gases such as CO, CO₂ and to a lower scale O₃ and NOₓ[3], that is not the case for volatile organic compounds (VOCs) and in particular BTEX (Benzene, Toluene, Ethylbenzene and Xylene). In the most recent review of sensors for the measurements of VOCs in ambient air [4,5], the authors concluded that the current sensor technology is not yet able to measure the concentrations expected in ambient air and that they generally suffer from poor selectivity.

Using the MACPoll Protocol of evaluation and calibration of low-cost gas sensors [6] which targeted low-costs sensors for inorganic gaseous, we present the evaluation of low-cost sensors and sensor based devices for benzene measurements. Indeed, the AQD defines as mandatory the monitoring of benzene in ambient air. In particular, it allows the use of indicative measurement methods but it requires the use of a selected method to meet a defined Data Quality Objective (DQO) of 30%. This DQO is defined as the relative expanded uncertainty of measurement and it shall be assessed in the region of the limit value (LV) of 5 μg/m³ for the annual mean.

2. Materials

Out of an extended review of the potential sensor candidate [5], a set of six commercially available sensors or research prototypes were selected. Table 1 gather the brand, the model and the
technology of the commercially available devices with their declared limit of detection and the experimental coefficient of determination of the linear regression. We also included in the evaluation process three devices that are part of research project. The first one uses a multi MOx/semiconductor sensor operated in Temperature Operation Cycle (TCO). The second one also uses TCO but with a SiC-FET sensor prototype. The last one is a miniaturized Gas Chromatograph based on PID sensor.

Table 1. List of commercial sensors and portable devices selected and coefficient of determination of the linear regression ($R^2$).

<table>
<thead>
<tr>
<th>Manufacturer/Institute</th>
<th>Model</th>
<th>Principle</th>
<th>Limit of Detection (ppm)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aeroqual</td>
<td>VM</td>
<td>Semiconductor</td>
<td>0.001 (resolution 0.0001)</td>
<td>0.00815</td>
</tr>
<tr>
<td>Ion Science</td>
<td>Tiger Select</td>
<td>Portable hand held based on PID sensors</td>
<td>0.010 (resolution 0.001)</td>
<td>0.8011</td>
</tr>
<tr>
<td>Mocon Baseline</td>
<td>item 045-014 (color Blue)</td>
<td>PID</td>
<td>0.00025</td>
<td>0.9924</td>
</tr>
<tr>
<td>Alphasense</td>
<td>PID-AH</td>
<td>PID</td>
<td>0.0005</td>
<td>0.89165</td>
</tr>
<tr>
<td>Membrapor</td>
<td>ETO/M-10</td>
<td>Electrochemical</td>
<td>resolution 0.05</td>
<td>0.9605</td>
</tr>
<tr>
<td>3</td>
<td>CH2O/M-10</td>
<td>Electrochemical</td>
<td>resolution 0.01</td>
<td>0.4040</td>
</tr>
<tr>
<td>University of Linkoping</td>
<td>Not available</td>
<td>MOS + TCO</td>
<td>Not available</td>
<td>0.8992</td>
</tr>
<tr>
<td>CNR-IMM Bologna</td>
<td>miniGC</td>
<td>Portable GC + PID</td>
<td>miniGC</td>
<td>0.3615</td>
</tr>
</tbody>
</table>

In a second stage, the performances of these sensors were evaluated under controlled conditions in an exposure chamber developed by the JRC. More details on this exposure chamber are described elsewhere [7]. This exposure chamber uses PID closed loop (Proportional, Integral and Derivative) in order to ensure the stability of the gaseous mixtures. The measurement of the levels of inorganic species was carried out by traditional analysers. For the organics species, a PTR-MS (Proton Transfer Reaction Mass Spectrometry) has been integrated as input of the PID loop [8]. A GC-PID 955 from Syntech was used in parallel as a reference measurement method to ensure selectivity, accuracy and traceability of the concentration of BTEX. All parameters are automatically and independently set and controlled. Conversely to other exposure chambers, the reference values of all compounds are measured allowing the full traceability to national/international units when evaluating sensors [7].

3. Methodology and Results

An extensive experimental design covering the evaluation of metrological parameters such as the response time, the repeatability, the lack of fit of calibration with hysteresis and short-term and long-term drifts have been applied. Meteorological interferences were also evaluated, in particular the effect of temperature, relative humidity, pressure and wind velocity. Finally, the cross sensitivity was characterized for the following interfering gaseous compounds: ozone, nitrogen oxides, carbon monoxide, toluene, xylene and five low-weight alkanes. This study gives preliminary results regarding the evaluation of the response time, the hysteresis in concentration, the influence of temperature, relative humidity and organic interfering compounds.

We evaluate the response time of sensors, $t_{90}$, considering the time needed by the sensor to reach 90% of the final stable value in both increasing and decreasing concentration. For this test, the set point of concentration was set to around 10 ppb of benzene and temperature and humidity were kept stable. The first observation was that the major part of the sensors was not able to detect such a low level of benzene. However, one PID sensor and the TCO MOx device showed a response time within the same range of the PTR-MS with $t_{90} = 6$ min. In this particular experiment, the miniGC prototype cannot be considered as it gives a measurement every 15 min. However, the miniGC shows a response time equal to the reference GC-PID 955 with $t_{90} = 35$ min.

The original calibration levels were included between 0 to 3 ppb of benzene by steps of 0.5 ppb in randomized order to take into account any possible hysteresis effects. Generally, calibration lines were found linear. Table 1 gives the coefficient of determination of the calibration lines. Except the
A semiconductor sensor and one electrochemical, all the sensors showed a high correlation with the reference measurements.

The effect of other organic compounds such as toluene, xylene, ethane, propane, butane and pentane was also evaluated in a 4 steps procedure: (1) the sensors were exposed to zero air; (2) they were then exposed to benzene alone; (3) the interferent was then injected and the concentration is either measured by the GC-PID 955 or estimated by dilution; (4) finally, 3 ppb benzene was added to the mixture, keeping the experimental conditions stables in order to ensure a stable level of interferent. The influence of each interfering compound was determined separately. The tests were carried out at 22 °C and 60% of relative humidity. Figure 1 gives an estimation of the sensor sensitivity compared to their response to 3 ppb on benzene.

As expected, the PID sensors (PID-AH and Tiger Select) showed the most important sensitivity to interfering compounds in terms of number of species. In particular they seem to be very sensitive to toluene, propane and butane. Both semiconductor sensors and the CH2O/M-10 showed a cross-sensitivity to alkane molecules and in a lower extend to toluene and xylene. A lower sensitivity was observed for the ETO/M-10 and the PiDTECH. The two devices which demonstrate the lowest interfering effect are the miniGC and the MOS + TCO.

The estimation of the dependence of sensors toward hysteresis was carried out using the calibration levels with a ramp of rising benzene followed with a ramp of decreasing levels and finally with another rising ramp. Three calibration lines were plotted, one for the 1st ramp of rising levels, one for the falling levels and one for the 2nd ramp of rising levels. Only the PID sensors and electrochemical cells seems to be affected by hysteresis of concentration. However, this effect will have to be validated against the short term drift in a later stage.

The influence of the changes of temperature or relative humidity on the sensor’s response were also studied. Two series of tests were conducted independently, generating ramps of temperature and humidity in a hysteresis cycle while gaseous levels in the chamber were kept constant. The ranges of temperature changed between 12 and 32 °C (by step of 5 °C) and the range of humidity was kept between 40% and 80% (by step of 10%). In general all the tested sensors showed a strong dependency to temperature and relative humidity characterised respectively by linear and quadratic regression lines. Only the miniGC showed to be totally independent from any temperature and relative humidity effects.
4. Conclusions

This laboratory evaluation shows that the current sensor technology is not able to accurately and selectively measure benzene at ambient levels. The PID sensors were generally found linear but they intrinsically suffer from high cross-sensitivity to other organic compounds. Amperometric and PID sensors seem also to suffer from a huge hysteresis effect. Finally, both amperometric cells and semiconductor sensors suffer from a lack of sensitivity and high dependency to relative humidity and temperature. Only the sensor based devices (miniGC and MOS + TCO) were able to reach an interesting sensitivity associated with an almost non-existent cross sensitivity towards other gaseous interfering compounds. During this laboratory experiments, other parameters such as the repeatability, the limit of detection, the short term and long term drift have been estimated. Also, the influence of inorganic gas such as carbon monoxide (CO), ozone (O3) and nitrogen monoxide (NO) and dioxide (NO2) have been studied. These last results are still under evaluation. The results presented are only valid for the sensors’ version under tests in the conditions and at the time of the tests.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors, EURAMET, had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References


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