Advantages and limitations of measuring BTEX with a commercial GC-PID system in-situ

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Abstract

The performance of a commercial gas chromatograph with a photo-ionization detector (Series 9100 GC-PID, MOCON, Lyons, Colorado, USA) measuring benzene, toluene, ethylbenzene and xylenes (BTEX) was evaluated during the winter of 2017 and spring 2018. The objective of this work was to determine the accuracy and precision of the equipment to measure BTEX concentrations in field conditions near oil and gas well pads and use the data in a health impact study.

The equipment was operated inside a mobile laboratory that provided semi-controlled environmental conditions. The instrument response was verified by analyzing gravimetric standards made at NOAA-GMD. Results show that the equipment presents a linear response for all species within the 0.5-54 ppb range (Figure 1).

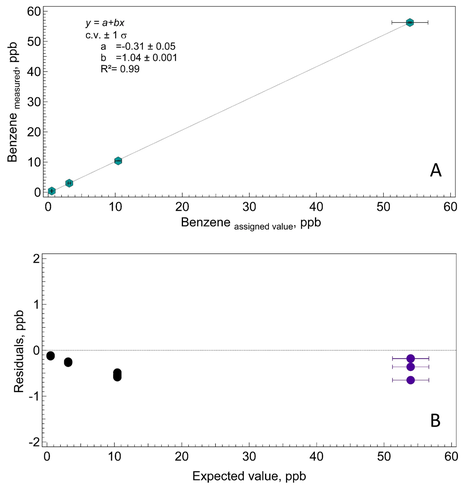

Figure1. A) Linear response of the 9100 done inside the mobile lab.

Figure 2. Residuals from linear regression (Figure 1) . **Black:** gravimetric standards. **Purple different parent source**

The instrument showed consistent results through the measurement period with the exception of certain events when temperature in the mobile lab changed dramatically.

The instrument

The Ametek-Mocon, Baseline 9100 is a gas chromatograph with a photo ionization detector, it was designed to measure compounds from sub-parts per million (sub-ppb) to percent levels.

Photoionization detector (PID) theory

Photo ionization is the process by which a photo-excited electron absorbs enough radiant energy to be ejected from the atom or molecule producing a flow of electrons and positive ions. The 9100 analyzer measures the the electron stream as a current that is proportional to the amount of VOC's in the detector and it reports that as a concentration.

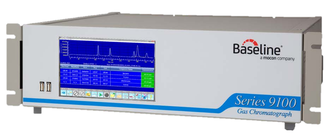

Figure 2. Baseline 9100

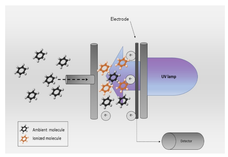

Figure 3 PID schematics.

Performance in the field

The analyzer was placed inside of a mobile laboratory that experienced extreme temperature variation. The operational temperature range of the 9100 is 0-40 ºC. Field conditions in the winter did not surpass the range, however the changes in temperature were large and abrupt. When such changes occurred the calibration and reference gases were not detected properly by the manufacturer's processing software or the concentrations were underestimated.

Performance in the field cont.

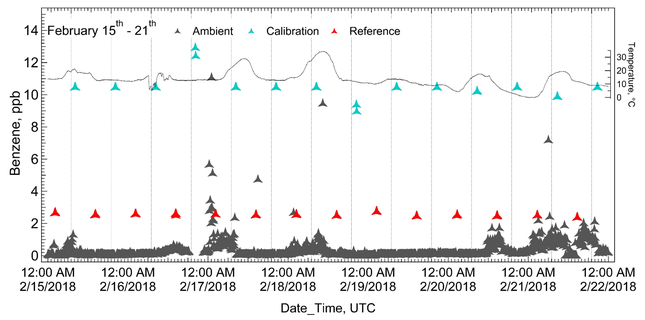

Figure 4. Example of data gathered in the field.

Instrument assessment

The 9100 was moved to a laboratory to asses its performance under controlled conditions.

Measurement range

Procedure:

The instrument measurement range was tested by measuring 13 tanks with known BTEX mixing ratios. Each tank was measured 5 times. Between each tank a reference gas was measured as well.

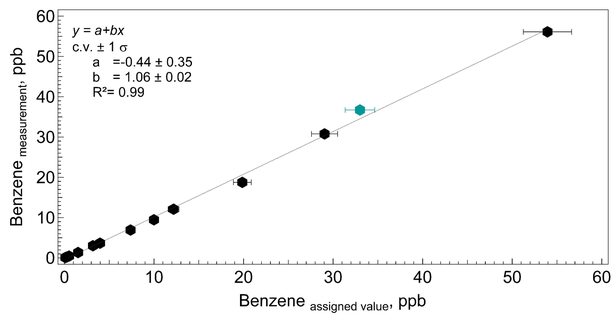

Figure 5. Laboratory test of measurement range of the Baseline 9100 using calibration gases.

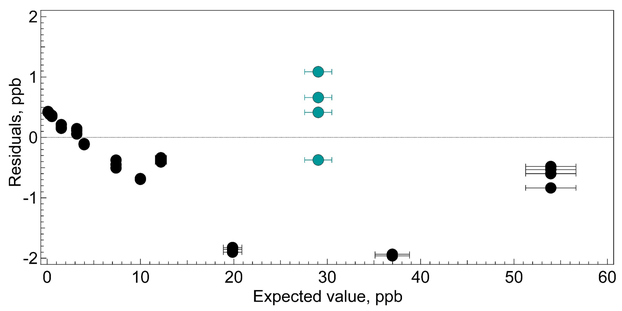

Figure 6. Residuals from laboratory test measurement range. **Black:** gravimetric standards. **Teal:** spiked tank with an approximate assigned value.

A.V.	0.102	0.281	0.514	1.52	3.18	3.97	7.38	9.99	12.188	19.86	29.04	33	53.94
Mean	0.080	0.235	0.451	1.33	3.01	3.65	6.91	9.45	12.09	18.74	30.78	36.72	56.11
S.D.	0.006	0.005	0.009	0.027	0.04	0.007	0.06	0.005	0.032	0.032	0.613	0.103	0.157

Table 1. Summary statistics of the measurement range test. N=4. A.V. Assigned value. S.D. Standard deviation

Hysteresis

Procedure:

The test consisted in measuring consecutively 3 different tanks with known concentrations: A nitrogen tank was used as a "zero" tank, and the concentrations for benzene were 3.18 ± 0.08 ppb and 12.18 ± .0.30 ppb .

Instrument assessment cont.

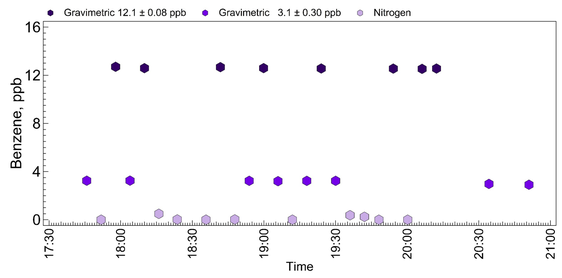

Figure 7. Memory test for Benzene. Other species show the same behavior.

Reproducibility

Procedure

We used a spiked tank with BTEX as a source for our sample. That would assure us to have the same concentration every time. Two different approaches were taken to measure the reproducibility. 1) 24 hour sampling with a calibration at the beginning and a calibration at the end of the test. 2) 24 hour sampling with a calibration every 8 hours.

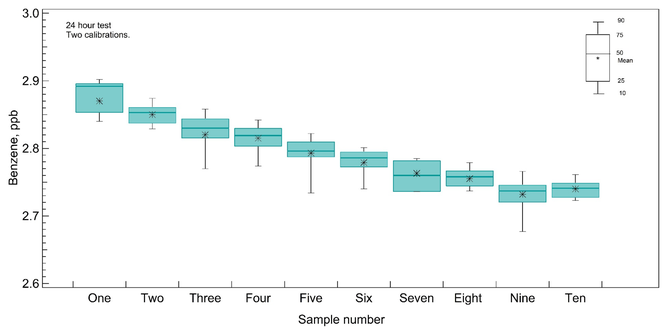

Figure 8. Reproducibility test. Two Calibrations. Each sample has 19 injections (N=19).

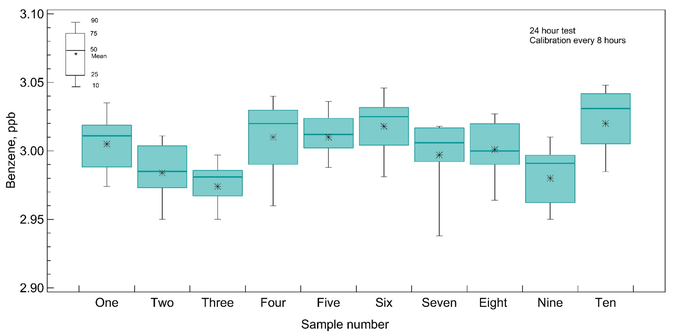

Figure 9. Reproducibility test. 2 Calibrations every 8 hours. Each sample has 19 injections (N=19) .

Results of this test show that the instrument requires frequent calibrations in order to reduce the variability in the measurement.

Conclusions

- The Ametek-Mocon, Baseline 9100 is a robust instrument to monitor ambient levels BTEX compounds.
- The effects of temperature in the quantification of the compounds is a difficult problem that needs to be resolved within the environmental.
- This instrument presents a calibration drift that can be resolved by increasing the frequency of calibrations.
- The large measurement range and the high frequency sampling will allow us to characterize the variability of background concentrations as well as ambient concentrations near oil and gas production operations.

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