

## ***Interactive comment on “Influence of environmental humidity on measurements of benzene in ambient air by transportable GC-PID” by Cristina Romero-Trigueros et al.***

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General comments.

The manuscript by Romero-Trigueros et al. address an important issue regarding air quality monitoring of benzene by transportable GC-PID. The tests are reported clearly and the implications discussed appropriately. However, my main concerns about the manuscript are:

1) Focusing on benzene: It would be more relevant to have investigated all the species analysed by this specific GC-PID, often referred to as "BTEX analyser" (for benzene,

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toluene, ethylbenzene, and xylenes).

Focusing on benzene is supported by the fact that this is the only VOC in the European Union with limit values and a standardized method for measuring its concentration in air. It is true that adding toluene, ethylbenzene and xylenes to our work would have improved the paper but these species were out of our goal. Measuring toluene, ethylbenzene and xylenes would have meant either repeating the tests for these species –increasing the project cost (more reference gases for each of them) and time; or having worked with a reference gas mixture with all these components, which would have increased the uncertainty of the mixture composition and its stability. For all of this and, mainly, because benzene was our target VOC, we only carried out the tests with benzene. Nevertheless, in the future, the rest of compounds could be further investigated.

2) Previously reported influence of pressure: A previous publication from the same authors in a different journal reported that data from this type of GC-PID might be affected by pressure difference. These issues hint at a disputable publication strategy spreading results of the characterization of this monitor in several manuscripts, increasing the publication count of the authors, but diluting the relevant information for the users of this type of monitors. Therefore, I would recommend to reject this manuscript.

We the authors think that Reviewer #1 has been a bit harsh with us. It is true that we have published another paper related to the influence of pressure on GC-PID benzene measurements. These two papers, together with many more tests that have not been published, are the results of a PhD thesis. We believe that those tests with interesting results should be published independently in order to be treated deeper. If all the tests were to be included and discussed in a single publication, its length would have been too long. This is, of course, our point of view and does not have to be shared by everybody. But, again, we do not think this is enough to reject our paper as the results in it have not been published anywhere else.

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- The content of the manuscript is well reflected in the abstract but it has been omitted that temperature influence has also been tested. Even though the result is that the temperature has no influence, it might be worth to emphasize this result in the abstract (or even in the title of the manuscript).

The reviewer is right and temperature influence should be mentioned in the abstract and could be also mentioned in the title of the manuscript.

- page 3, line 25-26: Tests with temperature should have their dedicated experimental section and the results should be reported only in section 3.2.

Temperature tests could be treated as a main goal of the manuscript together with humidity (accordingly to previous comment) and, therefore, the manuscript should change accordingly. This would mean adding a new sub-section in the experimental.

- page 4, line 7: It should be clarified (possibly in the introduction) that the EN Standard the authors are referring to citation "EU, 2008".

"EU, 2008" refers to Directive 2008/50/EC. "EN, 2015" refers to EN Standard 14662-3:2015 and this will be stated clearer in the introduction. However, the preliminary test in section 3.1 was carried out according to EN Standard 14662-3:2015, which is the previous version of the standard. This is because these tests were carried out before the release of the new version. Even though the tests measuring the humidity influence have changed in the new version of the Standard, this is not important as those tests only revealed a significant influence that was subsequently studied deeper by designing new experiments. In other words, for us, the Standard was only the starting point which revealed a significant influence of ambient humidity. From there, we carried out a deeper study of the influence of humidity in measurements.

- page 5, line 7: The sentence starting with "This influence has a negative sign,..." should be revised as the wording seems odd.

The wording will be changed to "This is a negative influence, that is, ..."

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- page 6, line 4-5: Statistics have been used but are poorly described in this one sentence. What is the value for  $p=0.05$  and 14 degrees of freedom and what are  $n_1$  and  $n_2$ ? This should be improved and clarified for readers that are not familiar with such statistic tools.

The information missing will be added (t-value for  $p=0.05$  and 14 degrees of freedom is 2.145 and  $n_1$  and  $n_2$  are the number of data in the least-square regressions of Figure 2 (for nominal benzene concentrations of 5 and 40  $\mu\text{g}/\text{m}^3$ , respectively). Also, a mistake was detected. Our calculated t-value is higher than the tabulated one which means that we reject the null hypothesis, that is, there are significant differences in the two slopes not attributed to random errors. This will be corrected in the final manuscript.

- page 6, line 20-24: It could be discussed in a bit more detailed how the results reported in the literature might have suffered from the presented influence of RH, given the reported environmental conditions of the measurements.

A thorough revision of literature has been carried out in order to find works where benzene was measured with a similar instrument to that used in this work. Many works use active or passive sampling followed by ex situ thermal desorption and GC-PID or GC-FID (e.g. Marc et al., 2016; Fracasso et al. (2010); Allou et al. 2008; Tran et al., 2000). There are a few of them that use in situ GC-FID (e.g. Zhang et al. 2017; Durana et al. 2006) and in situ GC-PID (e.g. Bruno et al., 2001; Kelessis et al., 2006; Villanueva et al., 2012). Bruno et al. (2001) and Villanueva et al. (2012) use gas chromatographs from Syntech Spectras so a study of the influence of humidity in their measurements could be done as long as calibration details and relative humidity data are provided. Bruno et al. (2001) mainly focused on source apportionment and they do not provide information related to ambient humidity. The average concentration of benzene during the sampling period was  $4 \pm 1.6 \mu\text{g}/\text{m}^3$  so measurements were close to the annual limit value but, mainly, below it, so around 2% bias is expected at 20 °C and 50% relative humidity if calibration was carried out with dry gases.

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Villanueva et al. (2012) intercompared tropospheric ozone, benzene and toluene by a commercial DOAS and conventional monitoring techniques. The instrument used to measure benzene and toluene was the same as the one used in our work. They mention the use of certified gas mixtures to calibrate their instruments. There is no mention to water vapour in the mixtures so it is assumed that they are dry gases. Their results show that average levels for ozone, benzene and toluene obtained with DOAS were higher than those obtained with UV photometry for ozone and GC-PID for the aromatics. The largest differences found are for benzene. Although the water interference found in our work is compatible with the results obtained in Villanueva et al. (2012), it does not explain the whole difference between the analytical techniques used.

These discussions could be added in the corrected manuscript.

- from page 6, line 25: This whole paragraph is a bit strange to me. It is not clear if the discussion is related to findings (or speculation?) of the authors or from the literature (in which case, references would be missing). The paragraph starts with "have been proved", but then rest reads like possible explanation for the observed influence of humidity on the results. Moreover, if the effect of water on preconcentration and chromatographic separation is not discussed (e.g. baseline, peak shapes, etc.) because is thought not to be relevant, this should be briefly motivated. Do authors expect the water concentration at the detector when benzene elutes to be the same as the ambient water concentration during sampling?

There was a missing reference that has been added (MSA, 2005). The technical document can be found in <http://media.msanet.com/NA/USA/PermanentInstruments/GasSensorsTransmitters/SaveToxSafeVOC/07-2092WhitePaperPID.pdf>

The baseline did not change when zero gas with different amount fractions of water vapour was measured. The peak shapes did not change either when measuring a

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constant amount fraction of benzene with different amount fractions of humidity. This is why we think that water vapour does not interfere in the preconcentration and separation steps. This will be included in the final manuscript.

Although the amount fraction of water vapour was not measured at the outlet of the instrument, it is assumed to be the same as the inlet, because this instrument does not have any dryer or scrubber.

- page 7, line 25: If "presumably" TEX are also affected, authors should at least mention briefly why they did not include them in their present work and if they are planning to do it in the near future. If they do have results for these compounds, they should not be withdrawn and included in the present manuscript.

As mentioned previously, these species were out of the scope of this work. We only studied benzene as it is the only VOC with limit values in air quality in the European Union. This will be stated clearer in the manuscript.

#### Technical corrections

- page 1, line 25: typo "h0ematologic" Thanks. This will be changed in the corrected manuscript.

- page 2, line 28: Trigueros et al., 2016 is missing in the bibliography It appears as Romero-Trigueros et al. and, therefore, it will be changed in the text.

- page 3, line 12-13: use either commas or long dash (–) to separate "the ratio of the actual mass of water vapour present in the sample to the mass of the dry air" The comma will be removed.

- page 4, line 5: replace "pressure" with "humidity" Thanks. This will be changed

- page 4, line 20: I suggest to use "with different absolute humidity (AH) values" The word "values" will be added to the sentence. Thank you.

- page 5, line 20: Word order: "the initial temperature of the sample being irrelevant in

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the whole process" Thank you for the suggestion.

- page 9, line 24: This is not a DOI, this is an URL. Thanks for this.

- page 9, line 32: Remove "http://dx.doi.org/". Thanks.

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