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Comment

## ***Interactive comment on “A new method for total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID)” by A. C. Nölscher et al.***

**Anonymous Referee #1**

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general comments

The article “A new method for total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID)” by Nölscher, et al. describes the use of a new instrument for the pyrrole detection in the CRM. This work is particularly interesting as the techniques available to measure OH reactivity are until now all expensive and bulky which isn't the case for the detection proposed here by GC-PID. As the OH reactivity is a key parameter to understand the oxidation processes taking place in the different atmospheric environments studied during field campaigns, this new combina-

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tion would permit to develop more instruments dedicated to this measurement. The title isn't maybe the most appropriated because the method used is the CRM, already used previously and only the pyrrole detection is different. I would propose to replace method by detection system. As the article is based on the use of detection by GC-PID, more technical and quantitative details would be useful on this technique as well as a more accurate quantification of the level of interference due to water or species potentially found in different environments and the effect on the reactivity measurement. The work presented in the article is of high quality and rigorous as it covers interference tests, comparisons with the detection by PTR-MS in laboratory with standard mixtures tests but also during two field campaigns in different environments even if longer comparison periods would have given more confidence. The data obtained during the HUMPAAC-COPEC 2010 gives encouraging results concerning the reliability of the GC-PID detection. The measurement capabilities, advantages and drawbacks of each detection system are well described and discussed. The improvements made on the CRM set-up are also detailed and give new, useful information for the potential new users.

#### specific comments

P3577, L28 : as one of the other OH reactivity techniques is called "pump-and-probe" and the pump part is described, it would be useful to add that the probe is made through a gas expansion and a LIF measurement at high repetition rate ( a few kHz) by the technique FAGE (Fluorescence Assay by Gas Expansion).

P3578, L22 : "Different combinations of reagent and detector can be chosen for the CRM according to the required instrumental characteristics." It would be interesting to have an overview concerning the combinations possible and already tested if existing.

P3582, L11 : the GC-PID used is described as "custom-built", is it possible to give information concerning the difference with the commercial instrument ? What is the availability of other instruments? Pertinent reference can be given for a description of

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the principle and specificities of this detection system?

P3582, L15 : could you give more details about the water filter ?

P3582, L16 : which type of column and the typical heating program used ?

P3583, L1 (Fig 1) linked also to the P3584, L6: the background level after the pyrrole peak is lower than after, is it due to the effect of the water peak ? Is it possible to add a chromatogram with humid air alone and the Gaussian fit used for the pyrrole ?

P3583, L5 : I don't understand the sentence, a deconvolution is needed ? Why the water peak is inverted ?

P3583,L14 : Estimation of the concentrations measured possible ? What would be the effect of species with a longer retention time than pyridine?

P3583,L19 : level detected in biomass burning can be indicated

P3583,L21 : time proposed between for the alternating ambient / reactivity measurement ?

P3583,L26 : why using R2 for the calibration and latter R for correlation between GC-PID and PTR-MS measurements ?

P3584,L8 (linked to figure 3) : the relative humidity used is low, what would be the effect of a higher humidity ? Will it change the offset or the slope ? Why a negative intercept in dry air ?

P3584,L11 : values for lengthening the chromatographic separation, tests done ? Effect on the area of the pyrrole peak ?

P3584, L16 (linked to fig 4) : What effect is expected due to the detector aging ? An offset change or a slope change ? No saturation effect for the peak at 175 ppb ?

P3584, L21 : how much time needed to do the maintenance ? Possible during field campaigns apparently as described P3588

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P3585, L13 : how the “no memory effect” of the pyrrole on the Teflon pump was tested ?

P3585, L16 : leak tests done ?

P3585, L20 : why the pump C2 is needed as there is MFC for zero air ?

P3586, L1 : what means “not too rapid” ? Range time?

P3587, L22 : how frequent ?

P3587, L24 : “Even during the influence of an aged biomass burning plume no pyrrole or pyrrole interfering peak could be detected (Sect. 2.3)”. Instead of referring to section 2.3, I would refer to mention the parallel measurements done with the second PTR-MS or the GC-PID during HUMPPA-COPEC from 26/07 to 29/07 and described in (Nölscher, 2012) Intercomparison within the canopy ?

P3588, L2 : how much time is needed for the GC-PID maintenance ? What is the cost for a new detector ? How often should it be replaced?

P3588, L20 : I don’t understand the name Pearson R, does it mean that the correlation coefficient  $r$  from a Pearson linear regression is used ?

P3589, L17 : Is it a scientific interest or more a technical limitation which explain why the conditions of GC-PID operation wasn’t set at the optimal conditions for the campaign in the plant chamber ? A detector cleaning wasn’t possible before the beginning of the campaign?

P3590, L12 (Table 2) : what is better to do for the GC-PID detection : to correct from the humidity level using a “short” chromatogram or to length it to suppress the effect ? What is the best compromise concentration accuracy / resolution time? In Table 2 : the inlet flow for the GC-PID isn’t continuous, what is the frequency? Does it involve instabilities?

P3591, L5 : is it possible to give a range of concentration and then the level of interfer-

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ence expected on pyrrole measurement in conditions described ?

P3592, L10 : Even if some interferences are suspected for OH measurements in some specific conditions, these interferences won't affect the reactivity measurement done by the FAGE coupled to a photolysis cell as the OH is generated at a determined time by a photolysis laser and the decay measured in a range of the second. If an interference producing a fake OH signal, then it will be in the background signal.

P3591, L18 : which technical improvement ?

P3591, L20 : how to diminish the water and toluene interference ? Will it change the resolution time ?

P3599, Fig. 1. /2. : why the max for pyrrole peak isn't at the same retention time (even if a.u linked to a real time in s) in Fig. 1 and 2. ? The separation conditions are different?

technical corrections

P3600, Fig 2. : Difficult to distinguish the different species with only the colored lines, compound names can't be added on top of the peak? P3601, Fig. 3. : a space missing between Standard and deviations

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