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Atmospheric
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Discussions

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.

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The authors are grateful for the detailed comments by referee 1. First, as suggested the title will be modified to: "Total OH reactivity measurements using a new fast Gas Chromatographic Photo-Ionization Detector (GC-PID)". Also the technical description of other OH reactivity instruments will be revised to a more accurate termination concerning the LIF (pump-and-probe) techniques.

1.1) General questions concerning the GC-PID technology are grouped and answered as follows below.

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 the principle and specificities of this detection system?

As example:

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

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

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

P3584, L16 (linked to fig 4) : What effect is expected due to the detector aging? An offset change or a slope change? the inlet flow for the GC-PID isn't continuous, what is the frequency? Does it involve instabilities?

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

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?

P3591, L18 : which technical improvement?

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

The presented Gas Chromatographic Photo-Ionization Detector is an instrument that has been built by Environics-IUT GmbH based on already existing VOC analyzers and optimized for the detection of pyrrole for use with CRM. Compared to commercially available systems sensitivity was improved, interferences were minimized, and the separation between peaks of interest (here: pyrrole) was optimized. The modifications were accomplished in collaboration with the company and the modifed version of this instrument is available for purchase.

A small sampling pump draws air continuously through the system. Due to a switching valve a short stop in this flow occurs after each sampling period, i.e. after each chromatogram. This does not produce instabilities in the pyrrole detection itself. For total OH reactivity measurements via CRM it has to be assured that this flow discontinuity does not affect the flows through the reactor. Within the GC-PID instrument, the sample first passes the particle filter. Then a short capillary gas chromatographic column, which is operated isothermally, separates VOCs and water. In the detection cell, molecules of the separated sample are ionized by UV light. Also material diffusing from tubing and other interior components get ionized and can cause an offset. Electrical noise of the detector adds to this and increases the offset in general. Water absorbs in the UV and shields energy available for ionization causing the signal in the detection cell to drop when leaving the column.

In the course of the GC-PID testing, it was found that with time the offset decreased and the sensitivity changed. Hence, both the intercept and the slope of a calibration varied with time. To be precise, there are two effects: 1) The detector ages and shows decreasing sensitivity towards any ions that are detectable in principle. 2) The PID window coats with pyrrole becoming more opaque with time. Hence, the UV light available for ionization decreases. These two effects result in decreasing sensitivity and an unfavorable signal to noise ratio.

To maintain the instrument's performance, the instrument was sent back to the company and it took ca. 5 days to do all necessary improvements and checks. Our instrument was sent back once in 1 $\frac{1}{2}$ years of intensive measurements (costs of a new detector: ~2500 €. Depending on handling and usage of the instrument maintenance frequency and costs may vary.

Future versions of the devices will be modified according to the experience reported here. The newest version is already smaller, lighter, better protected against water,

optimized to separate water (and other interfering components such as toluene) and pyrrole, and most importantly, the lamp as well as the PID window are easily accessible. This way, maintenance of the instrument during a field campaign can be performed by the operator at the site.

1.2) More specifically, comments dealt with details on the new GC-PID system.

Examples:

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?

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?

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?

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

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

P3584, L16 (linked to fig 4) : No saturation effect for the peak at 175 ppb?

P3590, L12 (Table 2) : What is the best compromise concentration accuracy / resolution time?

Figure 1 depicts an example of a typical GC-PID chromatogram for pyrrole. Between 500-1000 a.u. the signal dropped due to water and it increased to a peak between

1300-2000 a.u. for pyrrole. The offset for this specific chromatogram is slightly lower than 2000 counts, as can be seen for the beginning of the chromatogram, and the long period between water and pyrrole (separation for this chromatogram worked very well). It looks like the baseline did not come completely back to the same level after the pyrrole peak. This is because of the limited time given for the chromatogram. Two seconds more would show that the same background level was reached also after the pyrrole peak. For the final manuscript another example will be chosen and the Gaussian fit included. Since the separation between water and pyrrole works well for most times, both peaks are clearly visible so that including both in one figure seems reasonable.

By comparing Figure 1 and 2 it can be seen, that the pyrrole peak maxima appeared at different times. Depending on temperature, different sampling conditions and state of the instrument the retention time of pyrrole might slightly change with time. For analysis the software takes this effect into account and since pyrrole is the only peak to be integrated no problem occurs.

Since the separation between water and pyrrole works reasonably well (as can be seen e.g. in Figure 1) for most times, the integration of pyrrole is typically not affected by water. The example of Figure 3 shows how the integrated peak area of pyrrole increased due to humidity, when the peaks were not well separated. Depending on the size of the water signal pyrrole is overestimated by a factor which increases with higher humidity. The correction is easy to apply as long as humidity is measured alongside with the GC-PID. For independent measurements a good separation is mandatory. During our measurements a chromatogram length of 60-70 s provided reasonable good separation. For most accurate results, we additionally applied a correction factor if necessary.

As described in the text for Figure 2 the head space of liquid compounds was used to determine the retention times. Hence, an estimation of concentrations is not possible. Most probably concentrations were quite high, between a hundred ppbV to low ppmV

levels. For these high levels no saturation effect could be noted. Similarly, the 175 ppbV introduced for the pyrrole calibration, as seen in Figure 4, did not saturate the detector.

Blank tests subsequently after injecting extremely high concentrated compounds showed no defined peaks of the previous probe other than hysteresis. Late eluting peaks of the previous probe have little influence due to peak broadening. Hence, for ambient levels no interfering effect can be expected. For extremely high concentrations the baseline might bend slightly.

The tuning of the system will depend on the chemical condition at the measurement location and the exact nature of the scientific question. Averaging times, tuning for separation, software for integration, lengthening, shortening, sensitivity ect. can be adjusted to individual needs.

1.3) And a comment of general interest to the GC-PID total OH reactivity measurements was:

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?

The testing of a new device is based on both scientific interest and the desire to gain operational experience. The instrument was operated for the first time during two sequential campaigns after being run in the controlled conditions of the laboratory. The two campaigns served to show the rate of deterioration of the detector signal under field conditions which was not previously known. As we have stated, based on our experience a full maintenance of the detector is advisable prior to a campaign.

1.4) Similarly, the referee commented on the total OH reactivity method, the CRM in general:

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.

Indeed, different combinations are possible for detector and reagent for CRM total OH reactivity measurements. The newly developed GC-PID is an alternative for PTR-MS pyrrole detection, but in principle any other detection techniques are possible as well. We will further emphasize this point in the new manuscript with the hope of inspiring further practitioners to apply alternative detectors to this measurement.

The choice depends on the availability of instruments and the needs of the users, who decide which time resolution and accuracy is necessary for the field of application. When running the system with a different reagent following aspects have to be taken into account (Sinha et al, ACP 2008): The reagent reacts with OH at a suitable rate which is well known. An easy and accurate detection system should be available. Samples should not contain the reagent, so that no interferences complicate the measurements. Similarly no other interfering compounds should be present. Hence, the choice of a reagent strictly depends on the user’s needs. We find pyrrole reasonable for ground based ambient continental measurements. However, for biomass burning (high reactivity/pyrrole emissions), airborne based (high and low reactivity/temperatures) or marine studies (extremely low reactivity) a different reagent would be valuable.

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

The alternation time used for different campaigns may vary a lot depending on scientific interest, environmental conditions and instrumental set-up. Under boreal forest conditions C2 and C3 were modulated every half an hour and ambient background measurements (for investigating GC-PID interferences) performed several times a day.

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

The set-up as operated for the presented measurements for CRM included a sampling pump downstream of the reactor. This way, the ambient air sample was directly drawn into the reactor to react with the generated OH. This avoids contact of the ambient sample with the pump. With this, the pressure inside the reactor dropped slightly below ambient pressure (about 1-4 mbar). A mass flow controller for zero air used during C2 measurements pushes air into the reactor at about ambient pressure. In order to adjust C2 and C3 flows to the same levels an additional pump on the C2-side is needed to create the same pressure as for C3 measurements, i.e. slightly below ambient. This remark will be added to the manuscript for more clarity in the experimental set-up Section 2.4.

Various questions comment on the total OH reactivity measurement via CRM in detail, such as:

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

P3585, L16 : leak tests done ?

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

P3587, L22 : how frequent ?

Operating the CRM requires various tests and checks before actual measurements can start. Subsequent to the reaction of ambient air in the reactor with OH and the competitive reaction of pyrrole and OH, only pyrrole is of interest for detection. Hence, the sampling pump used for drawing air-samples through the reactor needs to be inert towards pyrrole. Tests were performed by comparing pyrrole levels before and after the pump. Leak tests were routinely done after set-up by injecting methanol at all connections and by checking flow rates each day. The catalytic converter was tested before and after measurements. Humidity was followed with the PTR-MS as well as with a humidity sensor probing the exhaust air of the CRM system. For extremely rapid humidity changes between two baseline measurements (C2), data was excluded from analysis later. Also the alternation between C2 and C3 was adjusted to the different campaign characteristics. In the case of the boreal forest measurements 2 modulations per hour were found to be appropriate. Chamber measurements are usually characterized by more stable parameters and therefore switching to the baseline could be done in extended time steps (i.e. less frequently). Ambient conditions can change more rapidly (e.g. within a couple of minutes), so the switching frequency could be shortened (e.g. 4-6 modulations per hour). For GC-PID operation, each day several background measurements were performed with ambient air to ensure that no interfering compounds were detected at the pyrrole retention time.

1.5) Technical question to the paper:

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

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 ?

Pearson R is used as a measure for the correlation between two variables. The quality of correlation between GC-PID and PTR-MS performance was described in Figures 7, 9 and 11. Standard tests showed very good agreement of both instruments with a Pearson R of 0.97. For the HUMPPA-COPEC campaign 2010 (Fig. 9) excellent correlation was found, with a Pearson R close to 1. The Jülich measurements showed less correlated detector results, with a Pearson R of 0.51. Still the correlation is positive, but due to low sensitivity in the GC-PID, high noise and low total OH reactivity values inside the plant chamber the correlation plot pictures a widely distributed cloud of values. For consistency, the R^2 in Figures 3 and 4 will be changed in the manuscript to the same measure, to Pearson R.

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

PTRMS or the GC-PID during HUMPPA-COPEC from 26/07 to 29/07 and described in (Nölscher, 2012) Intercomparison within the canopy ?

Indeed, a reference to the detailed analysis paper for the total OH reactivity measurements during HUMPPA-COPEC 2010 should be included here.

P3591, L5 : is it possible to give a range of concentration and then the level of interference expected on pyrrole measurement in conditions described ?

Unfortunately for this kind of question, but luckily for our measurements, we did not observe any interference during the measurements conducted in the laboratory, boreal forest and Jülich plant chamber. Hence, for these environments the GC-PID could perform without any significant interference. More tests and experience with direct biomass burning emissions (where pyrrole is likely to be present) will show how much ambient toluene or other pyrrole emissions could possibly influence the total OH reactivity measurement using CRM and the GC-PID. It should be noted, however, that the large mixing ratios of pyrrole used in this determination generally dwarf those of ambient VOC. The presented study can be seen as feasibility assessment of a new detection system for CRM total OH reactivity measurements, using a less expensive, more portable, less power consuming alternative to current measurement devices. Hence, completion and further development of the presented technique is mandatory.

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.

We agree. Still we think that it needs to be discussed and tested how interferences possibly disturb OH and total OH reactivity measurements using LIF based techniques (c.f. Mao et al. 2012, ACPD).

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

Both these minor remarks will be taken into account in the new version of the presented manuscript. This way, the paper will be improved providing a useful addition to the existing literature concerning total OH reactivity measurement techniques.

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