

Interactive comment on “Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air” by C. Hak et al.

C. Hak et al.

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The authors would like to thank the referee and have taken into account the comments raised.

Specific Comment 1: “The authors pointed out that zero adjustment was performed between once per day (IFU) and 6 times per day (BUW). It would be interesting to know the effect of changes in zero signals (and that of the calibration signals) on the results of the Hantzsch instruments. It is therefore recommended to include the change in “response factors” as function of time in the paper.”

Reply to Comment 1:

The change of the zero air signal is not caused by the zero air scrubber (as suspected by the referee), but due to chemical changes of the Hantzsch reagent.

The zero adjustment and/or zeroing interval and calibration interval of the Hantzsch technique depend on the degradation of the operation solutions. To keep the solutions as stable as possible it is recommended to keep the reagents in a refrigerator and to add a HCHO trap to the venting line of the storage container of the stripping solution. With these measures that were done in the campaign for all instruments we can guarantee a zero drift of less than 30 pptv per day and a span stability within 24 hours within 2%. Working without the HCHO zero trap at the stripping solution container results in a baseline drift of up to two ppbv per day depending on ambient concentration levels and dimensions of the liquid container.

There were no systematic changes in the response factors of the instruments. For the PSI instrument it was within 3% (1sigma) during the four days of measurements. The calibrations of the BUW instrument were also stable within 5% for the three calibrations performed.

Specific Comment 2: “It is reported that the ozone scrubber is omitted for technical reasons for the DNPH-cartridge sampling in the morning and in the evening hours, respectively. The authors conclude that there is no problem with ozone on the DNPH formaldehyde results due to the lack of additional peaks in the HPLC-chromatograms. Can co-elution of the signals be ruled out from concurrent sampling with and without ozone scrubber.”

Reply to Comment 2:

Considering the comment, we will change the paragraph on page 2911 (lines 19 to 23) to the following:

Positive interference in the form of a number of extraneous peaks in the HPLC-UV

chromatograms has been reported for C18 DNPH-cartridges, when used at high atmospheric ozone concentrations without ozone scrubber [Vairavamurthy, 1992]. In the present study, sampling without ozone scrubber was only carried out at low ozone concentrations. Thus, positive interference is unlikely. Moreover, no extraneous peaks were monitored. However, as in all kinds of chromatographic analysis, coelution of unknowns with the target analytes cannot be excluded. In previous studies of ambient air from this area, we have used the DNPH technique at low ozone concentrations without ozone scrubber and have been able to rule out interference from potential coelutants by analysis of the DNPH extracts not only by HPLC-UV but also with HPLC coupled to atmospheric pressure mass spectrometry [Duane et al., 2002].

Specific Comment 3: “The authors reported an excellent correlation between the Hantzsch instruments of BUW and PSI but an offset of around 20% for unknown reasons. They argued problems dealing with the “zeroing” of the monitors. This hypothesis could have easily been tested using the built-in formaldehyde permeation source of the Hantzsch monitors (for example by comparing the zero signals of synth. air and of scrubbed synth. air + formaldehyde from the permeation source). It is therefore recommended to include tests of proper function of the formaldehyde scrubbers as part of the regular operation procedure of the Hantzsch monitors.”

Reply to Comment 3:

We agree with the referee that the zero signal might be a problem. The suggestion to include regular tests of the formaldehyde scrubber in the operation routine can be confirmed. Such a test was done prior to the campaign with all the instruments operated by IFU. During the campaign, only the quality of the zero baseline was monitored. A damaged scrubber results in poor instrument performance and drifting and an unstable zero baseline.

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Reply to Technical Comments:

- 1) In the header of Table 1 we shifted the '[min]' to the adjacent cell 'Time res.'
- 2) As suggested we have changed the size of Figure 2. In detail, we increased the height of Figure 2d and we will suggest to the production office to use two columns, i.e. the complete width of the page, for this figure.
- 3) We have omitted the numbers in Fig. 6, as was suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 2897, 2005.

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