

***Interactive comment on* “Technical Note:  
Determination of formaldehyde mixing ratios in  
polluted air with PTR-MS: laboratory experiments  
and field measurements” by S. Inomata et al.**

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We thank valuable comments and suggestions from the referee. Responses to the comments and suggestions are given below. We reflected these responses in a revision of the manuscript.

1. We revised the sentence according to the comment.
2. The residence time of the sampling inlet tube is estimated approximately to 6 s, however, the loss of HCHO in the sampling inlet tube was unknown.
3. We did not operate the MFC of the dilution flow at the lower end. As shown in the insert figure of Fig. 3, flow rates were varied. In addition, the MFCs used in the

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dynamic dilution device were calibrated by the film flow meters as mentioned in the text.

4. In this paper, we used the measured detection sensitivity to determine the mixing ratios of HCHO in air. We mentioned the calculated sensitivity here to compare with the results reported by Steinbacher et al. (2004), who used the calculated values, assuming the rate constant of  $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The backward reaction prevents the formation of  $\text{HCHOH}^+$  ions. The reaction rate constant for the backward reaction ( $k_{-6}$ ) increases 5 times from  $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with the increase of the E/N ratios from 108 to 162 Td while the reaction time decreases only 33%. Therefore, we mentioned that the backward reaction becomes important, especially at high E/N in the drift tube.

5. When the normalized signal intensity of "s" is obtained for HCHO in the dry conditions, the mixing ratio of HCHO is determined by  $s \text{ (ncps)}/4.9 \text{ (ncps/ppbv)}$  at  $U_{\text{drift}} = 520 \text{ V}$ . When the sample passes through the dynamic dilution device, the ion signals decrease down to  $s \text{ (ncps)}/2.7$  in the present study and the estimated mixing ratio by the calculation is derived from  $s \text{ (ncps)}/2.7/7.0 \text{ (ncps/ppbv)}$ . A ratio of  $s/2.7/7.0$  to  $s/4.9$  is 0.26. This value should be compared with 0.21 obtained from Steinbacher et al. (2004).

6. Time dependence of concentrations of  $\text{HCHOH}^+$  ions is described as follows:

$$[\text{HCHOH}^+] = k_6 [\text{H}_3\text{O}^+] [\text{HCHO}] / (k_{-6} [\text{H}_2\text{O}]) [1 - \exp(-k_{-6} [\text{H}_2\text{O}] t)] \quad (\text{A})$$

If the equilibrium does not occur at the end of the drift tube, we should fit the data shown in Fig. 4 by

$$y = a / (x + b) [1 - \exp(-4 \times 10^{13} \times f \times k_{-6} \times t \times (x + b))] \quad (\text{B})$$

When  $f = 1$ , we could not obtain good results of the fitting. Then, we varied the value of  $f$ . When  $f$  is 2.9, we obtained fitting parameters  $a$  and  $b$  of  $(1203 \pm 140)$  and  $(6.0 \pm 2.5)$

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for  $U_{drift} = 400$  V,  $(521 \pm 44)$  and  $(8.7 \pm 1.3)$  for  $U_{drift} = 520$  V, and  $(251 \pm 22)$  and  $(5.6 \pm 1.0)$  for  $U_{drift} = 600$  V. An agreement of b-values at the different E/N conditions was improved, however, we can not explain the meaning of the factor f. When we use this empirical value of f of 2.9, values of  $4 \times 10^{13} \times f \times k_{-6} \times t \times (x+b)$  for  $x > 2.1$  mmol/mol are  $> 1.1$  in the case of  $U_{drift} = 400$  V,  $> 3.2$  in the case of  $U_{drift} = 520$  V, and  $> 3.4$  in the case of  $U_{drift} = 600$  V. Except a few data points at  $U_{drift} = 400$  V, we think that we can ignore the second term of Eq. (B).

However, we should mention that the non-equilibrium situation may cause the disagreement of b-values at different E/N conditions in the text.

7. Slashes (/) were missing at  $\delta\alpha_{49}/\alpha_{49}$ ,  $\delta\alpha_{33}/\alpha_{33}$ , and  $\delta\alpha_{47}/\alpha_{47}$ . We decided not to use percentages. (We removed Table 2.)

8. We revised Fig 6 according to the comment.

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