



Supplement of

Instrument intercomparison of glyoxal, methyl glyoxal and NO_2 under simulated atmospheric conditions

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$Y \downarrow X \rightarrow$	CE-DOAS	BBCEAS	Mad-LIP	FT-IR ^b	W-DOAS	SPME	CE-DOAS ^d
CE-DOAS							
Slope							
Int ^c	-	1.032(2)	1.301(3)	1.02(3)	1.090(4)	1.05(12)	1.02(1)
\mathbf{R}^2		0.005(2)	-0.06(2)	-0.1(7)	0.07(1)	0.01(1)	-0.17(1)
		0.9997	0.9998	0.999	0.9998	0.996	0.998
BBCEAS							
Slope	0.970(2)	_	1.2631 (8)	0.95(2)	1.048(1)	1.02(12)	0.97(1)
Int	-0.005(2)		-0.008(2)	0.5(6)	0.029(10)	0.00(2)	0.04(18)
\mathbf{R}^2	0.9997		0.9998	0.997	0.9998	0.996	0.999
Mad-LIP							
Slope	0.768(2)	0.7917(5)	_	0.77(2)	0.836(1)	0.74(8)	0.77(1)
Int	0.06(2)	0.006(2)		0.2(4)	0.06(1)	0.03(1)	-0.05(18)
\mathbf{R}^2	0.9998	0.9998		0.997	0.9994	0.995	0.9996
FT-IR ^D							
Slope	0.98(3)	1.05(2)	1.31(3)	_	1.07(2)	1.1(4)	1.03(10)
Int	0.1(7)	-0.6(6)	-0.3(5)		0.0(4)	-0.3(41)	-1(3)
\mathbf{R}^2	0.999	0.997	0.997		0.999	0.96	0.998
W-DOAS							
Slope	0.917(3)	0.955(1)	1.197(2)	0.93(2)	_	0.93(10)	0.92(2)
Int	-0.06(1)	-0.028(9)	-0.07(2)	0.0(4)	-	-0.08(3)	-0.02(20)
\mathbf{R}^2	0.9998	0.9998	0.9994	0.999		0.995	0.999
SPME							
Slope	0.95(10)	0.98(11)	1.35(15)	0.9(3)	1.07(12)		1.0(2)
Int	-0.01(1)	-0.00(2)	-0.04(2)	0.3(36)	-0.08(4)	-	0.0(14)
\mathbf{R}^2	0.996	0.996	0.995	0.96	0.995		0.994
CE-DOAS ^d							
Slope	0.98(1)	1.04(1)	1.30(2)	0.97(10)	1.08(2)	1.0(2)	
Int	0.17(10)	-0.05(19)	0.1(0.2)	1(3)	0.02(24)	0.0(14)	-
\mathbf{R}^2	0.998	0.999	0.9996	0.998	0.999	0.994	
^a Number in parenthesis is the 1- σ fit error of the last displayed digit							
^b Correlations for high concentration data only							
^c Units of the intercept are ppbv							
^d CE-DOAS fitting for weak band range							

Table S1: Correlation Matrix for experiment E1.^a

$Y{\downarrow} X{\rightarrow}$	CE-DOAS	BBCEAS	Mad-LIP	FTIR	W-DOAS	SPME
CE-DOAS						
Slope		1.035(5)	0.919(4)	1.01(3)	1.092(8)	1.2(1)
Int b	-	0.013(3)	-0.011(3)	0.2(1)	0.08(2)	0.00(2)
\mathbf{R}^2		0.9998	0.998	0.992	0.998	0.998
BBCEAS						
Slope	0.967(5)		0.9141(9)	0.95(2)	1.027(3)	1.1(1)
Int	-0.012(2)	-	-0.030(2)	0.0(1)	0.02(1)	-0.01(2)
\mathbb{R}^2	0.9998		0.998	0.992	0.997	0.998
Mad-LIP						
Slope	1.088(4)	1.094(1)		1.02(2)	1.057(3)	1.3(1)
Int	0.012(2)	0.033(2)	-	-0.1(1)	-0.05(1)	0.01(1)
\mathbb{R}^2	0.998	0.998		0.96	0.96	0.996
FTIR						
Slope	0.99(2)	1.05(2)	0.98(2)		1.08(2)	1.3(2)
Int	-0.2(1)	0.0(1)	0.1(1)	-	0.0(1)	-0.2(3)
\mathbf{R}^2	0.992	0.992	0.96		0.987	0.994
White-cell						
DOAS						
Slope	0.916(7)	0.973(3)	0.946(3)	0.93(2)		1.1(1)
Int	-0.07(2)	-0.02(1)	0.05(1)	0.0(1)	-	-0.3(1)
\mathbb{R}^2	0.998	0.997	0.96	0.987		0.998
SPME						
Slope	0.85(8)	0.88(9)	0.75(7)	0.8(1)	0.9(1)	
Int	0.00(1)	0.01(1)	-0.009(10)	0.1(2)	0.3(1)	-
\mathbf{R}^2	0.998	0.998	0.996	0.994	0.998	
^a Only data from	daytime experime	nt with defined le	evels; ^b Intercept	in ppbv		

Table S2: Correlation Matrix for experiment E8a.^a

Table S3: Correlation Matrix for the methyl glyoxal experiment E2."						
$Y {\downarrow} X {\rightarrow}$	CE-DOAS	BBCEAS	Mad-LIP	FTIR	W-DOAS	PTR-MS
CE-DOAS						
Slope a		0.990(3)	0.714(3)	0.852(9)	1.03(3)	0.813(3)
Int	-	-0.35(2)	0.02(2)	-0.55(12)	0.0(3)	0.86(2)
\mathbb{R}^2		0.9987	0.997	0.996	0.96	0.96
BBCEAS						
Slope	1.010(3)		0.720(3)	0.854(9)	1.05(3)	0.820(4)
Int	0.36(2)	-	0.38(3)	-0.02(10)	0.3(3)	1.25(3)
\mathbb{R}^2	0.9987		0.996	0.994	0.96	0.96
Mad-LIP						
Slope	1.400(6)	1.388(6)		1.16 ± 0.02	1.45(5)	1.093(7)
Int	-0.03(3)	-0.53(4)	-	-0.6 ± 0.1	-0.2(4)	1.22(3)
\mathbb{R}^2	0.997	0.996		0.995		0.96
FTIR						
Slope	1.174(13)	1.17(1)	0.86(1)		1.20(8)	1.04(3)
Int	0.65(13)	0.02(12)	0.5(1)	-	1.1(8)	0.3(2)
\mathbf{R}^2	0.996	0.994	0.995		0.97	0.97
W-DOAS						
Slope	0.97(3)	0.95(3)	0.69(2)	0.84(6)		0.84(3)
Int	0.0(3)	-0.3(3)	0.1(3)	-0.8(7)	-	-0.3(4)
\mathbb{R}^2	0.96	0.96	0.95	0.97		0.92
PTR-MS ^b						
Slope	1.231(5)	1.220(6)	0.915(6)	0.96(3)	1.19(4)	
Int	-1.05(2)	-1.53(4)	-1.12(3)	-0.3(2)	0.4(4)	-
R^2	0.96	0.96	0.96	0.97	0.92	

Table C2. ED a 0 . . 1 1 1

^a Number in () is the 1 sigma standard deviation for the last reported digit ^b PTR-MS data filtered for ramp up and odd section that bumps higher than the trend in all of the other instruments and assumes a 5% uncertainty in the 1 minute PTR data.

31



34 Figure S1: Absorption cross-sections of species measured by visible light absorption

35 spectroscopy instruments (Here convolved to FWHM = 0.5 nm, Mad-LIP (0.001 nm) and

36 BBCEAS (0.18-0.26 nm) both use much higher resolutions). NO₂ (Vandaele et al., 2002) and

37 water (Rothman et al., 2009) absorb in the same region as glyoxal (Volkamer et al., 2005),

methyl glyoxal (Meller et al., 1991) and biacetyl (Horowitz et al., 2001).



40 41 Figure S2: Non-calibrated PTR-ToF-MS signal showing the methyl glyoxal signal (m/z =

- 42 73.0284) and the neighboring water cluster (m/z = 73.0656). Subtracting the water cluster
- 43 interference and applying the calibration for methyl glyoxal yields the plot in Figure 2, Panel D.



46 Figure S3: Sensitivity of methyl glyoxal to high levels of NO₂ from experiment E10. Chamber

47 dilution has been scaled relative to concentrations at 14:10 from the decay of the SF_6 tracer. See

48 text for details.

49



50 Time of Day (UTC)
 51 Figure S4: Experiment E7, oxidation of isoprene under high NOx conditions. Panel (A) shows

52 the evolution of NO₂, isoprene, methacrolein (MACR) and methyl vinyl ketone (MVK) in the

53 chamber; Panel (B) shows methyl glyoxal, hydroxyacetone and glycolaldehyde; Panel (C) shows

54 glyoxal. The vertical dashed line indicates the chamber opening (09:32).



56 Figure S5: comparison of glyoxal measurements <0.5 ppbv during the start of Experiment E6

57 (08:20-08:45 and 10:30-14:00 UTC). Mad-LIP points in the middle of the plot occur during the

- 58 filling of the chamber with ambient air. The data during the filling period is subject to
- 59 inhomogeneities and has therefor been filtered.



61 Figure S6: Dependence of retrieved glyoxal mixing ratios from CE-DOAS (gold) with respect to

62 NO₂ concentration relative to values measured by Mad-LIP during the first 3 hours of

63 Experiment E6 (Δ Glyoxal = Cavity instrument – Mad-LIP). The data from the chamber filling

has been omitted in the fits (this data is shown in the grey points). Due to the arrangement of the

fans in the chamber, incoming ambient air during filling comes from the top of the chamber and

66 is first seen by the Mad-LIP instrument and then mixed into the rest of the chamber. These data

67 do not represent a well mixed chamber and thus have been omitted (see Fig. S10). Trends are on

the order of those measured during Experiment 9, but are still within the measurement

69 uncertainty. The larger symbols with variability bars represent the data binned by 2 ppbv bins in

NO₂. Fitted trends are to the actual data (as fitting the binned data would disproportionally

71 weight the data that had very few data points between 2 and 6 ppbv).





Figure S7: (A) Timeseries of glyoxal from E5. The morning consisted in stepping up the O₃

concentration in the chamber while varying the inlet tubing lengths to the various instruments.

75 O_3 was then flushed from the chamber (12:40-15:20) til the concentration was ~250 ppbv after

which C_2H_2 was injected (20 ppmv). Glyoxal increases sharply once C_2H_2 is injected (14:32

77 UTC) into the chamber containing O_3 (in absence of any TME). (B) Correlation plot for all

glyoxal data, and the low concentration points (inset), illustrating some evidence for nonlinearity at high concentrations, and bias at low concentrations that affected fitting of Mad-LIP

4 at a, but not the other instruments. Fitting Mad-LIP versus CE-DOAS yielded an offset of 330 \pm

81 20 pptv for an un-weighted linear fit, 205 ± 3 pptv for Mad-LIP if a weighted linear fit and $220 \pm$

82 20 pptv if a 3^{rd} order polynomial fit is applied.



Figure S8: Time series of glyoxal experiment 8a (A). Overnight dilution experiment E8b (B and C, same time scale). The decay of glyoxal in the chamber follows an exponential decay as the chamber is flushed. The data used in Figures 9 and 10 for evaluating the detection limits and precision are taken from the (grey shaded) period between 2 AM and 6AM. Values below zero cannot be shown on the logarithmic plot in panel C; however, as panel B shows, the data were generally scattered around zero within the range of the instruments' detection limits.

91



95 Figure S9: Sensitivity tests to quantify the small potential for calibration bias for glyoxal

96 measurements by CE-DOAS. See text for details.



98 99 Figure S10: Experiment E7 shows the CE-DOAS mixing ratio respond to the opening of the chamber roof (dashed line) before the BBCEAS and Mad-LIP measurements. There are no 100 offsets in time for the NO₂ signal (not shown), but similar delays in concentration changes upon 101 102 opening the chamber at low concentration levels are observed also in E5 and E6 suggesting a 103 chemical reason affects the inhomogeneity of the chamber at low concentrations. A fit to the 104 BBCEAS data that ignores the baseline data has a correlation of 0.98 but a large offset of 0.19 ppbv and an R^2 of 0.91 compared to the much better correlation found in Table 5. 105

106 **Description of CE-DOAS error propagation**

107 The overall uncertainty of the CE-DOAS comes from a combination of the errors in the

108 measurement. The contributing errors are as follows: Mirror Reflectivity (±2%), pressure

109 measurement (±0.5% full scale range of pressure sensor), temperature (±0.01 K), physical

110 lengths of the cavity (d_0 , full cavity length 92.0±0.1cm; d_s , sample cavity length, 79±0.2 cm) and

111 the absorption cross-sections (glyoxal, $\pm 3\%$ (Volkamer et al., 2005); NO₂ $\pm 3\%$ (Vandaele et al.,

112 2002)). The relevant equations are as follows:

113
$$C_{gly} = SCD_{gly}/L_{eff}$$
 (S1)

114
$$L(\lambda) = \frac{d_s}{1 - R(\lambda) + \alpha_{Ray}^{Air} d_0 + \sigma_{O_4} N_d^2 O_{2,mixing ratio}^2 d_s + \sigma_{NO_2} c_{NO_2} d_s}$$
(S2)

115 where the symbols and abbreviations are explained in the main text. In equation (S2) only the O_4

and NO_2 terms are considered to affect path length; a similar term could also be added for

117 glyoxal self-limitation. The calculation is considered at a wavelength that has low O_4 absorption.

- 118 An initial value for the glyoxal (or NO₂) concentration is retrieved from Eq. (S1) using Eq. (S2)
- 119 with no initial value for NO₂/glyoxal (Rayleigh case). For this case, the $\delta L_{eff} = 1\%$. For high NO₂
- 120 cases (Experiments E9 and E10) the fit error for the SCD_{gly} is on the order of 15% and dominates

121 the error, regardless of the uncertainty in the cross-sections or the use of iterations. For the cases

122 of glyoxal correlation experiments (Experiments E1 and E8a) the fit error is 1.5-2.0% over the

123 full range of glyoxal concentrations investigated in absence of interfering species. At this low

124 level of fit uncertainty the iterative solving of equations (S1) and (S2) to derive an accurate path

125 begin to matter. We consider the first and second iteration, after which further iterations lead to

126 changes smaller than 1%.

127 Sensitivity tests: RMS noise and effect of convolution on CE-DOAS calibration

128 Fig. S9 makes an attempt to quantify the uncertainty in the calibration of CE-DOAS, and assess

129 calibration bias due to transferring the literature cross-section to the actual instrument resolution

130 (convolution). An example spectrum of glyoxal, recorded at 11am during E8a, is shown in panel

- 131 (A); 1-3 ppbv, S/N = 180-300. The literature cross section was adjusted for resolution by
- 132 convolution with the measured line function of a Kr atomic line emission lamp (FWHM = 0.56
- 133 nm at 450.2 nm). Further tests were conducted, where the literature cross section was convoluted
- 134 with an artificially broadened line function of 0.616 nm FWHM (10%) and 0.84 nm FWHM
- 135 (50%). Tests were performed using two different convolution programs that are widely used in
- 136 the DOAS community (QDOAS, WinDOAS (Fayt and Van Roosendael, 2001)). Panel (B)
- 137 shows the fit residuals for the six cases investigated, that each used a different set of reference
- 138 spectra. Panel (C) compares the time series of the retrieved RMS residual noise (1-sigma) for
- 139 these case studies with the theoretical RMS noise that is expected for photon-shot noise limited

- 140 (white noise) spectra; see eq. (2) in Coburn et al. (2011). The RMS photon shot noise calculated
- 141 for the specific case of the spectrum shown in (A) was 2.33×10^{-4} absorbance units (a.u.), which
- 142 is near identical with the observed RMS = 2.39×10^{-4} a.u. RMS noise is indistinguishable (< 1%)
- 143 for the FWHM_{measured} and FWHM_{10%-bias} cases; significant residual structures remain for the
- 144 FWHM_{50%-bias} case, for which the observed RMS is a factor of \sim 3 higher than RMS_{shot-noise}. The
- absence of systematic structures in the measured RMS, and the agreement with the RMS
- 146 expected from theory demonstrate that the glyoxal absorption is well accounted for by CE-
- 147 DOAS, and that the instrument is operating in the photon-shot noise limit.
- 148 We have quantified the effect of FWHM-bias on the retrieved SCD. Panel (D) shows the relative
- 149 SCD deviation [calculated as 'deviation = $(SCD_{QDOAS} SCD_X) / SCD_{QDOAS} * 100'$]. Such
- 150 deviations in the SCD are found to be much smaller than the effect on RMS. For the 50%-bias
- 151 cases, the RMS increases by a factor of ~3, and SCD deviation is smaller 6%. Also shown is the
- 152 glyoxal SCD, which varied by a factor of 5 over the time period shown here. The relative SCD
- 153 deviation is independent of the glyoxal SCD. Finally, panel (E) shows that the relative SCD
- deviation is reasonably well approximated as a linear function of FWHM difference [= FWHM_X
- 155 0.56]. From the equation shown in Fig. S9E, and the uncertainty in our measured FWHM of
- 156 0.01 nm FWHM, we estimate that the overall bias from convolution of the literature cross-
- 157 section to calibrate CE-DOAS spectra is less than ~0.5%.
- 158 The overall uncertainty in the CE-DOAS calibration is 3.5%, and dominated by the uncertainty
- 159 in the literature cross section (~3%), with minor contributions from fit error (~1%), convolution
- 160 (0.5%), and iterative solving for path lengths (1.5%). Based on the excellent agreement with the
- 161 other instruments, we conclude that the possibility of other effects that can influence error (due
- 162 to gas-transfer efficiencies, and sampling lines) do not appear to be limiting the overall error
- 163 under the experimental conditions probed in this study.
- 164 **References**
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