Supporting Information

for

A new portable instrument for online measurement of formaldehyde: from ambient to mobile emission sources

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Text S1. Measurement principle

The basic chemical principles of the Hantzsch-Abs are based on the Hantzsch reaction (R1) and absorption photometry. In brief, liquid-phase HCHO reacts with acetyl acetone and ammonia to produce 3,5-diacetyl-1,4-dihydrolutidine (DDL), which specifically absorbs light at 415 nm.

$$HCHO + NH_3 + 2CH_3COCH_2COCH_3 \rightarrow DDL + 3H_2O \quad \text{(R1)}$$

Text S2. System description and operation

Abbreviations:

SS	Stripping solution;	**OF1 and OF2**	Optical fibers
DS	Derivatization solution	**MC**	Insulated metal capsule equipped with temperature-control device
SC	Stripping coil	**MP1 to MP4**	Micro solenoid pumps for liquid handling
CD	Cooling device for cycling water	**WT**	Water trap
HR	Heated reactor	**WF**	Water filter
DB	Debubbler	**MFC**	Mass flow controller for air sampling
LWCC	Liquid Waveguide Capillary Cell	**AP**	Air pump
LS	Light source	**MT**	Mixing tee
PD	Photodiode detector	**SP**	Syringe pump for waste handling

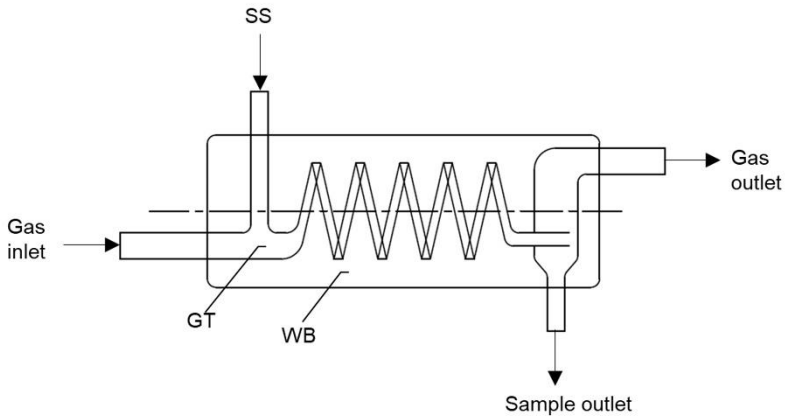
The zero air is provided by passing the ambient air through a filter cartridge containing a Hopkalit catalyst during baseline monitoring and calibration (not shown in Figure 1). All the tubes for gas are made up by 1/4'' Teflon tubes while those for solutions are by 1/16'' Teflon tubes. The Hantzsch-Abs consists of five modules including the sampling module, the reaction module, the detection module, the liquid delivery module, and the data acquisition and system control module. The whole system is contained in a case machined from an aluminum block (440×440×130 mm).

The data acquisition and system control module includes two 5V power supplies (LRS-350-5, MEAN WELL ELECTRONICS CO., LTD.), a 12V power supply (LRS-350-12, MEAN WELL ELECTRONICS CO., LTD.), a main control circuit board, a data acquisition and storage circuit board and a 7-inch touch panel coupled with a 32-bit ARM Microcontroller (CortexM3 STM32F103VET6). The touch panel is embedded for user operation, data acquisition, and visual display through a user-modifiable program. This module acquires data from the PD through a 16-bit analog-to-digital card. Data are exported through a USB or RS232 port to the user's computer. This module also governs the temperatures, MPs, SP, AP, and mass flow controller (MFC). The temperatures are monitored using high precision temperature probes PT100 and maintained constantly by PID. Data exports through the USB or RS232 to personal computer.

The liquid delivery module consists of four solenoid micro-pumps MPs (Bio-Chem Valve Inc., Boonton, NJ, USA) and one syringe pump SP (NKP-DA-S04Y, Karmoer).

84 The operating time of the solenoid micro-pumps delivering the solutions and samples
85 is fixed at 0.2 second while the turn-off time is alternative and flexible to maintain
86 different flow rates. The first MP (MP1) is set at a flow rate of 0.5 mL/min; this MP
87 aspirates and dispenses the stripping solution (SS). The third MP (MP3) is fitted at the
88 same flow rate; this MP delivers derivatization solution (DS). The second MP (MP2)
89 aspirates the sample solution downstream of the SC, mixes that solution with the
90 derivatization solution, and dispenses the resulting solution into the HR. The fourth MP
91 (MP4) delivers the reaction product into the detection module. Resulting liquid waste
92 is vented through a syringe pump SP.
93 In the sampling module, the air is driven by an air pump AP (DC 24V, Nidec) and
94 then the extraction of the HCHO occurs in a glass stripping coil SC. The gas flow rate
95 is set at 0.7 L/min and the residence time of the sampled gas passing through the SC is
96 approximately 0.2 s. Construction of the SC is shown in Figure S1. The stripping
97 solution SS and the air are brought into contact continuously in a flow manifold at the
98 beginning of the coil. A glass tube (inner diameter 3 mm), coiled in five spiral turns
99 (coil diameter 22 mm), is applied to the stripping of ambient HCHO. The visualization
100 design allows us to examine if the AP and MPs work well during operations. At the end
101 of the coil there is a gas–liquid separator connected where gas and liquid flow are
102 separated. Stripping solution and sample solution are controlled through MP1 and MP2.
103 Temperature is controlled at 20°C with cycling water in a double wall glass cylinder
104 WB cooled by a simple refrigeration unit CD, in order to prevent inaccuracies in

105 sampling caused by fluctuating external temperatures. A water trap WT for gas-liquid
106 separation and a water filter WF are further connected to the coil before the air pump
107 to protect the pump.



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109 **Figure S1.** Construction of the glass stripping coil. GT, glass tube; WB, water bath.

110 In the reaction module, derivatization solution DS is delivered by MP3 and mixing
111 with sample solution from MP2 in a Y-type mixing tee MT (ID 1.5mm). Then the
112 mixtures are aspirated into the heated reactor HR. The HR is made of 2 m 1/16'' (ID
113 1.0mm) PTFE tubing twined on a stainless-steel cylinder embedding a heating rod and
114 a temperature sensor. The residence time of the reaction solutions in the HR is
115 approximately 94 s at a liquid flow of 1.0 mL/min for sufficient reaction. The whole
116 assembly is put with insulating foam inside a plastic enclosure to make sure the
117 temperature is constant.

118 Reaction product goes through a tiny debubbler DB made of glass and then is driven
119 by MP4 to a filter with 1μm PTFE membrane (Acrodisc CR 25mm Syringe filter with
120 1μm PTFE Membrane, Pall Filter Co., Ltd.) before proceeding to the detection module.

The detection module mainly includes a Liquid Waveguide Capillary Cell (LWCC, 0.55 mm I.D., World Precision Instrument, FL, USA), a light source (LS), a photodetector (PD, λ=150~550 nm，λp=440 nm, Thorlabs, USA), two silica optical fibers (OFs, 400 μm diameter) and an insulated metal capsule (MC) equipped with temperature-control device. LS is composed of a high-intensity light emitting diode (LED, 415 nm, Luxeon Star, USA) and a low power instrumentation amplifier (INA129UA, Texas Instruments Inc., USA). A narrow-band filter (415 nm, Spectrogon, Sweden) is placed in the PD to reduce scattered light. Inside the LWCC, 415-nm light emitted by the LED entered the intersection port through OF1 connecting with the liquid line. Light and product solution is vented through another intersection port; Light then goes through OF2 and is detected by PD while sample solution discharges as waste. Optical signals are converted into voltage signals after detected. To avoid temperature fluctuations leading to refractive index variations of the sample solution and absorption fluctuations of light, the LS and PD are embedded in a dark metal box MC and kept in a constant temperature of 35 ^{o}C.

Better response together with lower deviation can be obtained when the liquid flow rates of stripping solution and derivatization solution are close to each other (see Figure S2). As a result, we generally chose a rate of around 0.5 mL/min comparable to the Hantzsch-Flu both for the two solutions to ensure more sensitive response. The reaction temperature also has significant effect on the response because higher temperature leads to shorter reaction time and more sensitive response as shown in Figure S3. It is easy

to generate bubbles if the temperature is too high, so a reaction temperature of 75 ºC is available and suitable.

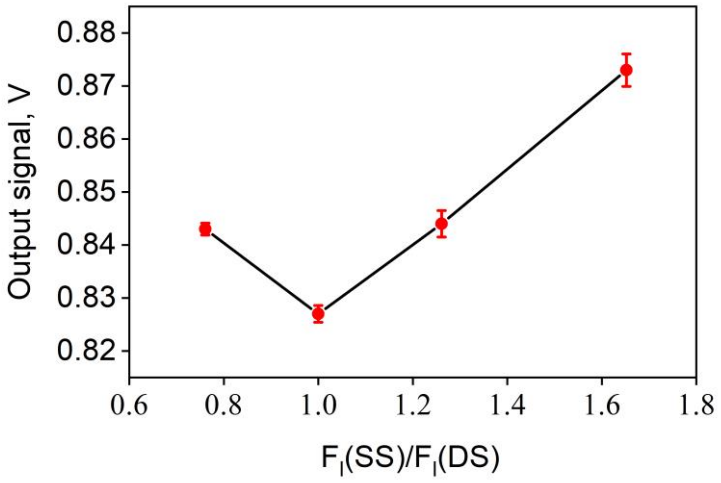

Figure S2. Signal response versus different ratios of liquid flow rate between of stripping solution, F_l (SS) and derivatization solution, F_l (DS). Liquid flow rate of stripping solution was fixed at 0.5 mL/min.

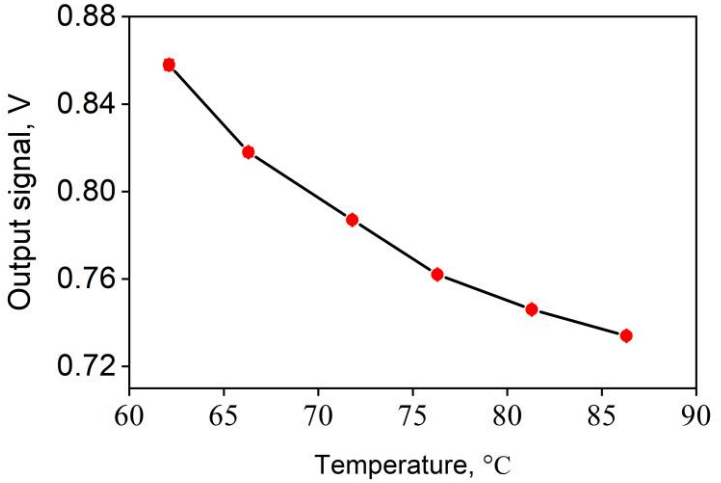

Figure S3. Signal response versus temperature of the reactor.

Text S2. Reagents

The stripping solution (SS) was 55 mmol/L H_2SO_4 by 15 mL sulfuric acid (95%~98%, Guaranteed Reagent, XILONG SCIENTIFIC) dissolving in 5 L Milli-Q water (18.2 MΩ cm at 25 °C, Millipore). Derivatization solution (DS) was prepared by mixing 10 mL acetyl acetone (99%, Analytical Reagent, XILONG SCIENTIFIC), 12.5 mL acetic acid (99.5%, Analytical Reagent, Beijing Chemical Works) and 385g ammonium acetate (98%, Analytical Reagent, XILONG SCIENTIFIC) in 5 L Milli-Q water (18.2 MΩ cm at 25 °C, Millipore). The derivatization solution was stored refrigerated at 10 °C to stabilize for more than 12 hours before use. For uninterrupted operation, stripping solution and derivatization are necessary to be replaced every six days.

Text S3. Calibration and calculations

The photodetector response was measured by delivering standard solutions of HCHO (within the linear detection range of 0 – 100 μg/L) through MP1 and sampling zero air during calibrations. The standard solutions were highly diluted solutions of a high-concentration stock HCHO solution dissolved in stripping solution and prepared fresh before use. The stock solution was prepared by diluted 500 μL 37% HCHO solution (37% solution in H2O, stabilized with MeOH, J&K Scientific) to 500 mL with Milli-Q water (18.2 MΩ cm at 25 °C, Millipore) and kept in a refrigerator. According to the Lambert-Beer law (Eq. (1)):

$$A = Log_{10}\frac{I_0}{I} = \varepsilon lc \quad (1)$$

The concentrations VS. $Log_{10}\frac{I_0}{I}$ was linear curve, where A denotes the absorbance signal, I_0 represents the average output signal (V) of zero air, I is that of HCHO solution at certain concentration, ε is the molar extinction coefficient, l is the optical path length and c is the concentration of HCHO (mol/L). Routine calibration of the instrument is conducted by working standard solutions of HCHO with concentration range of 0 – 100 μg/L (corresponding to 0 – 60 ppbv). The correlation for the linear fit of the calibration curve can be better than 0.99 (R^2) as shown in Figure S4.

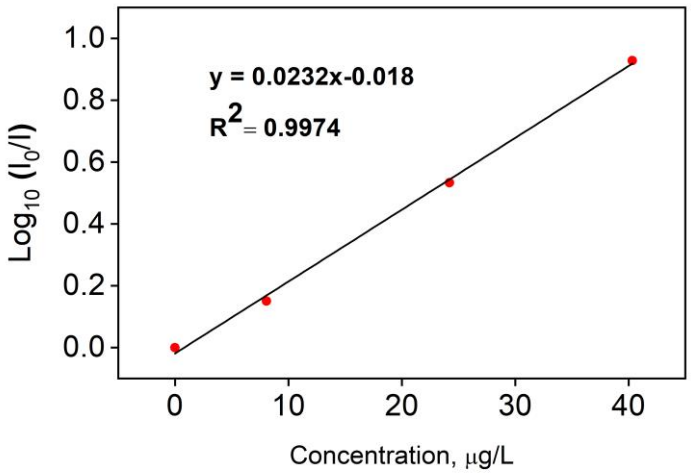

Figure S4. Calibration of the Hantzsch-Abs by HCHO standard solutions.

From the HCHO concentration in the liquid sample ($C_{[HCHO]}$, μg/L), the ambient mixing ratio of HCHO (C_{HCHO}, ppbv) can be calculated by the following Eq. (2):

$$C_{HCHO} = \frac{C_{[HCHO]}F_l RT}{M_{HCHO}F_g P\gamma} \quad (2)$$

where, P denotes the atmospheric pressure (101kPa), M_{HCHO} (g/mol) is the molecular weight of HCHO, T (K) is the sampling temperature and γ is the real sampling efficiency.

Text S4. Sampling efficiency

Laboratory experiments were carried out to determine the sampling efficiency of the stripping coil. Diluted HCHO gases were sampled using a Hantzsch-Abs connected to the commercial Hantzsch-Flu instrument in series. HCHO gases were generated and diluted using a Dynacalibrator (Model 500, Valco Instruments Co. Inc., USA) with Dynacal permeation devices (FORMALDEHYDE-PARA, 15 ng/min ± 50% at 50°C and 201 ng/min ± 50% at 70°C, Valco Instruments Co. Inc., USA). High-purity nitrogen (N_2) was used as a carrier gas. The liquid flow rate (F_l) was held constant at 0.5 mL/min; the sampling temperature of the stripping coil and the reaction temperature were maintained at 20°C and 75°C, respectively. Derivatization solution was stored in a refrigerator at 10°C. The sampling efficiency (γ) was deduced by comparison of HCHO concentrations observed using both instruments, using the following Eq. (3):

$$\gamma = \frac{C_1}{C_2 + C_1} \times 100\% \qquad (3)$$

where C_1 denotes the concentrations (ppbv) of HCHO observed by the Hantzsch-Abs and C_2 (ppbv) denotes the concentrations observed by the Hantzsch-Flu. The sampling efficiency of the Hantzsch-Abs was calculated to be 98.5 ± 0.1% under a

typical gas flow rate of 0.7 L/min, which is comparable to the sampling efficiency of the commercial Hantzsch-Flu instrument.

Text S5. Stability and sensitivity

Baseline drift is a common problem that affects the stability and sensitivity of Hantzsch methods. We applied an LWCC with an optical path length of 50 cm and an internal volume of 125 μL to the Hantzsch-Abs. The maximum voltage signal output from the Hantzsch-Abs was 3.3 V (under no absorbance); we chose 68% of the maximum voltage as the baseline signal. After 12 h of continuous baseline monitoring (system blanks, obtained by sampling no gas, averaged 2.26 ± 0.01 V), baseline signals dropped marginally, by 0.7%; this was within a reasonable range for long-term monitoring. However, we recommend baseline monitoring at the beginning and end of every measurement period, or every 12 h during continuous long-term measurements, to reduce the effect of baseline drift. The drift is corrected based on the gradient subtraction between the averaged concentrations calculated from baseline monitoring before and after each measurement as the following Eq. (4):

$$[HCHO]_{corrected} = [HCHO]_{original} - zero_1 - \frac{zero_2 - zero_1}{Gt} \times Dt \quad (4)$$

Where, $[HCHO]_{corrected}$ is the HCHO concentration corrected for the drift, ppbv; $[HCHO]_{original}$ is the HCHO concentration without correction, ppbv; $zero_1$ is the averaged zero concentration calculated from baseline monitoring before measurement,

ppbv; $zero_2$ is the averaged zero concentration calculated from baseline monitoring after measurement, ppbv; Gt is the duration of the measurement, s; Dt is the data acquisition frequency, s.

The liquid-phase performances at 18.5, 37, and 74 μg/L HCHO, determined by quickly switching between HCHO solutions and stripping solution, are shown in Figure S5. The time resolution (i.e., the time the instrument needs to rise from 10% to 90% of the full signal, t_{10}–t_{90}) was approximately 100 s, calculated using 10–90% of the full signal after a change in concentration. The delay time (the time the instrument needs to rise from 0 to 90% of the full signal, t_0–t_{90}) was 150 s. The relative standard deviation calculated from three consecutive measurements ranged from 0.3% to 0.7%.

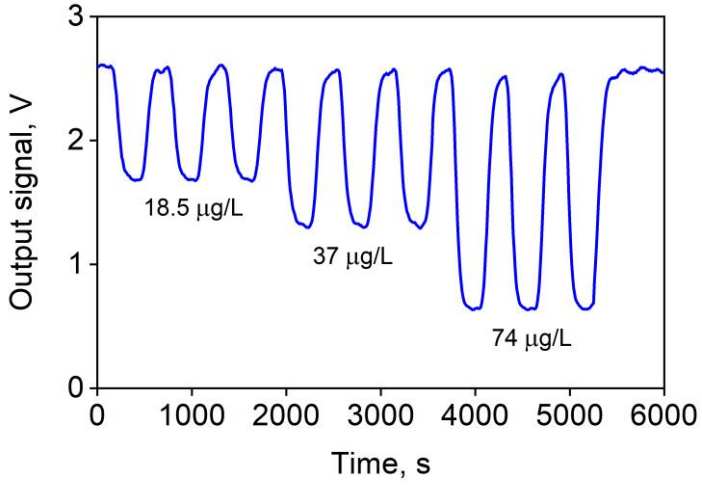

Figure S5. Liquid phase system performance by switching the HCHO solutions and stripping solution.

Text S6. Interference by other compounds

Interference by other compounds in the air, such as other oxygenated VOCs, is a contentious issue when utilizing Hantzsch methods. We conducted laboratory experiments to explore potential interference by acetaldehyde, acetone, and ethanol. We defined relative interference (α) as the interference signal and measured this parameter as HCHO concentration (ppbv) divided by the mixing ratio of the interfering compound (α = 100 × [ppbv-signal HCHO/ ppbv-compound]). All values corresponded to typical operating conditions under a gas flow rate of 0.7 L/min and a liquid flow rate of 0.5 mL/min.

Acetaldehyde interference was determined using acetaldehyde solutions ranging from 15.6 to 78.0 μg/L (corresponding to 6.7–33.3 ppbv in the gas phase). Each solution was tested for 20 minutes and solutions were prepared by dissolving an acetaldehyde solution (40% solution in H_2O, J&K Scientific) in 40 μg/L HCHO standard solution. Interference was below the limit of detection at a concentration of 6.7 ppbv, whereas concentrations of 16.6 and 33.3 ppbv led to HCHO signals of 0.4 and 0.3 ppbv (α of 1.7% and 1.1%), respectively. Ethanol solutions were prepared by dissolving ethanol (99.9%, ACS/HPLC Certified, J&K Scientific) in 40 μg/L HCHO standard solution. Ethanol had no detectable signal at 9.5 and 47.4 μg/L (3.8 and 19 ppbv); however, at 94.8 μg/L (38.0 ppbv), ethanol resulted in an average HCHO signal of 0.5 ppbv and α of 1.8 ± 1.1%. For acetone, interference was measured for 1 h using diluted acetone calibration gas (800 ppbv in N_2, Messer, Germany) using a Dynamic Gas Calibrator

(Model 146i, Thermo Fisher Scientific Inc.), and was determined to be 0.3 ± 0.2%. These results indicate minor interference effects from acetaldehyde, alcohol, and acetone on HCHO measurements at ambient levels.

Table S1. Interferences from acetaldehyde, acetone and ethanol.

Species	Concentration (liquid phase)	Concentration (gas phase)	Signal HCHO	Interference (α)
Acetaldehyde	15.6	6.7 ppbv	ND	ND.
	39.0	16.6 ppbv	0.4 ppbv	1.7 ± 1.8%
	78.0	33.3 ppbv	0.3 ppbv	1.1 ± 1.6%
Ethanol	9.5	3.8 ppbv	ND	ND
	47.4	19.0 ppbv	ND	ND
	94.8	38.0 ppbv	0.5 ppbv	1.8 ± 1.1%
Acetone		800 ppbv	1.4 ppbv	0.3 ± 0.2%

Text S7. Performances of the measurement ranges and time resolution using reactors in different lengths

We tested the HCHO solutions ranged from 0 to 180 μg/L under 20-cm and 50-cm reactor cells, which is shown in Figure S6. According the calibration curves, the measurement ranges of 20-cm and 50-cm reactor cell are determined to be 0 – 510 and 0 – 270 μg/L (corresponding to approximately 0 – 160 ppbv and 0 – 300 ppbv), respectively. We also tested the time resolution ($t_{10} - t_{90}$) using a 20-cm reactor cell, which showed a result of 90s.

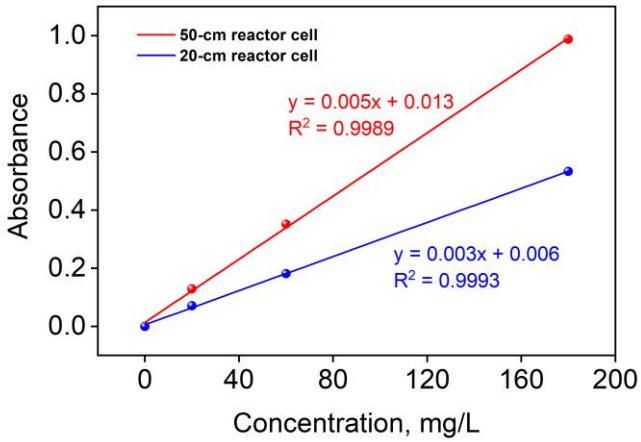

Figure S6. Calibration curves under different lengths of reactor cell.

Text S8. Power, size and weight of the Hantzsch-Abs and comparison with other instruments

The whole system is contained in a case machined from aluminum block AL coated by PTFE with a size of 440×440×130 mm. It weighs around 10 kg. Maximum power consumption by the instrument is 220 VAC, 300 watts.

Table S2. Comparison of the Hantzsch-Abs and other commercial instruments

	The Hantzsch-Abs	The Hantzsch-Flu	PTR-Tof-MS	FTIR[1]
LOD	25 pptv	100 pptv	~100 pptv	0.15 – 1.1 ppmv
Detectable range	Max 3 ppmv (adjustable)	Max 1 ppmv	Max 1 ppmv	/
Delay time/ Response time	150 s	300 s	100 ms	≤ 1 s
Size	440×440×130 mm	450×150×560 mm	600×910×800 mm	660×1970×970 mm
Weight	10 kg	20 kg	125 kg	250 – 450 kg

Power consumption	Max 300 W	110W	1500 W	max. 4.4 kVA

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279 **Text S9. Location and deployment of field observation**

280 The field observation campaign was located at Pingyuan Meteorological Bureau in
281 Pingyuan County, Dezhou City, Shandong Province, China (37.15°N, 116.47°E) which
282 is shown in Figure S7. The PTR-Tof-MS was placed in field container #1 with a
283 sampling inlet 1 mm in diameter. The Hantzsch-Flu and Hantzsch-Abs were placed
284 together in field container #2 and shared the same sampling inlet, which was 0.25 inches
285 in diameter. Both sampling inlets were approximately 3 m above the ground and placed
286 a few meters apart (Figure S8).

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288 **Figure S7.** Siting of field measurement.

Figure S8. Containers of field measurement.

Text S10. Diurnal variations of HCHO and acetonitrile concentrations

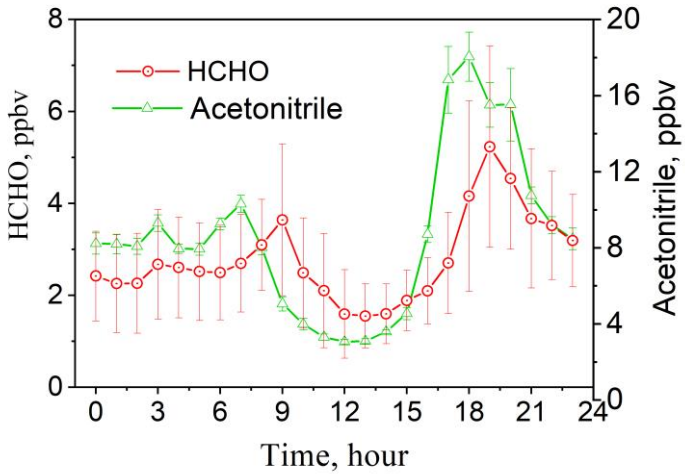

Figure S9. Diurnal variations of HCHO and acetonitrile concentrations during December 15 and December 21.

Text S11. Description of the sampling and pretreatment system

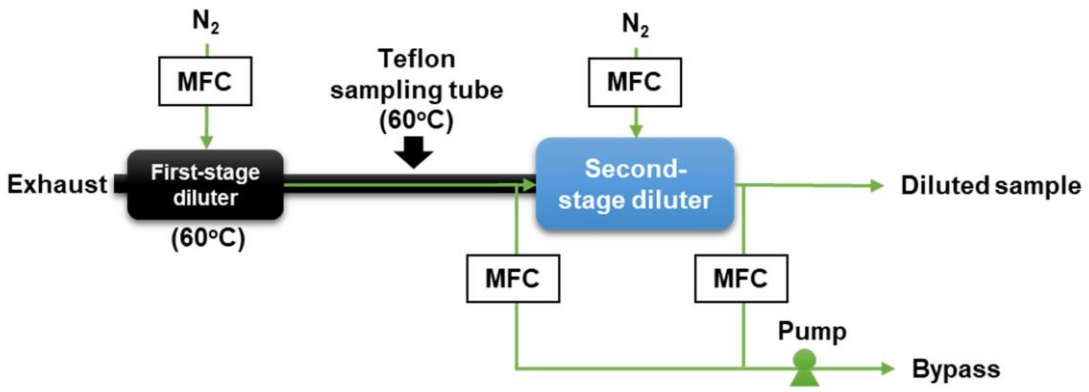

Figure S10. System schematic for the sampling and dilution system. MFC, mass flow controller.

The sampling and dilution system includes two diluters, Teflon sampling tube, four mass flow controllers (MFC) and an air pump. The first-stage diluter is embedded near the sampling port at the Teflon sampling tube, and both of them keep at an elevated temperature of 60°C, which can prevent the loss of HCHO due to rapid condensation of the exhaust. The sampling tube wrapped in thermal insulation material not only reduces the loss of HCHO due to rapid condensation of the exhaust but also avoid the effects of light. The second-stage diluter is following the Teflon sampling tube, offering a higher dilution for the sample. Nitrogen (N_2) is used as the dilution gas and regulated by MFCs into the two diluters. Exhaust is driven by the pump and regulated by another two MFCs set in the bypass, so that the sample would not be affected by MFCs. By adjusting the MFCs, the dilution ratio can be set up to 100.

Text S12. Test vehicles

Table S3. Specifications of the test vehicles.

	Light-duty diesel truck	Light-duty gasoline vehicle
Emission standard	China III	China V
Odometer, km	173046	/
Engine capacity, L	2800	1587
Exhaust control	None	Three-way catalyst
Fuel injection system	Common-rail Direct Injection	Multi Point Injection

314

315

Reference

(1) Suarez-bertoa, R.; Clairotte, M.; Suarez-bertoa, R.; Clairotte, M.; Arlitt, B.; Nakatani, S.; Hill, L.; Winkler, K.; Kaarsberg, C.; Knauf, T.; et al. Intercomparison of Ethanol , Formaldehyde and Acetaldehyde Measurements from a Flex-Fuel Vehicle Exhaust during the WLTC Intercomparison of Ethanol , Formaldehyde and Acetaldehyde Measurements from a Flex-Fuel Vehicle Exhaust during the WLTC. *Fuel* **2017**, *203* (May), 330–340. https://doi.org/10.1016/j.fuel.2017.04.131.