

Supplementary Information

A novel tandem of thermal desorption carbon analyzer and Off-Axis Integrated Cavity Output Spectroscopy for aerosol stable carbon isotope ratio measurement

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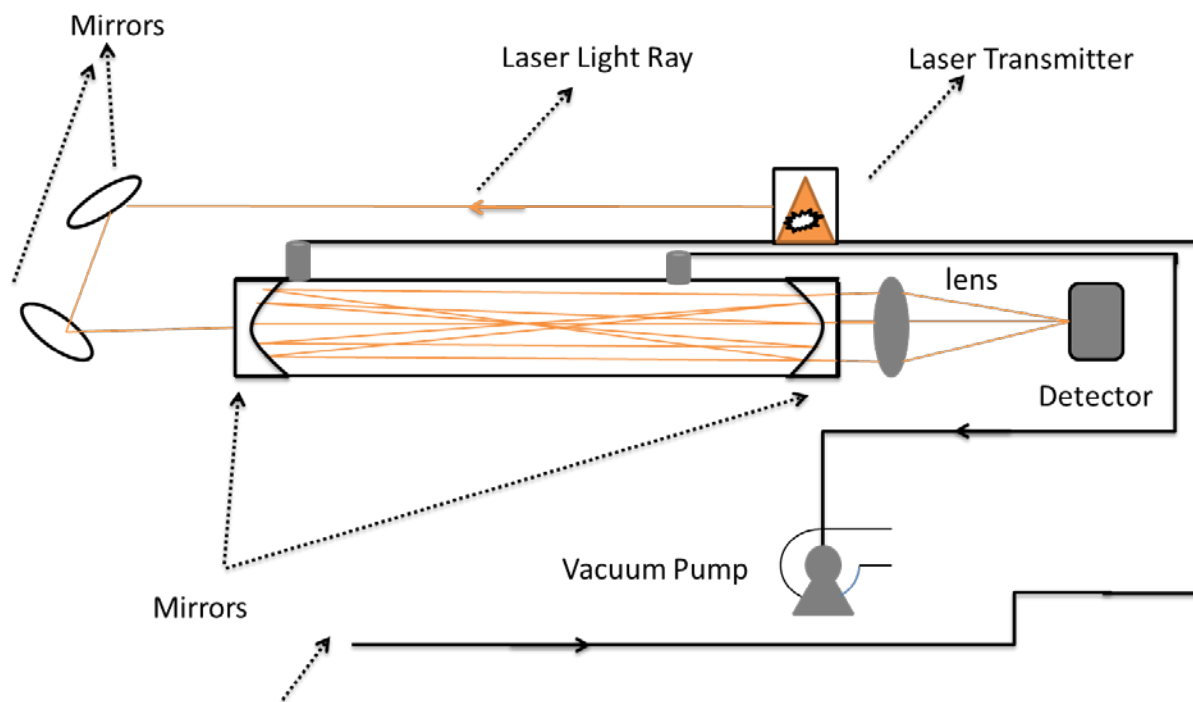


Fig S1: A schematic of working principle of Carbon Dioxide Isotope Analyzer (CCIA)

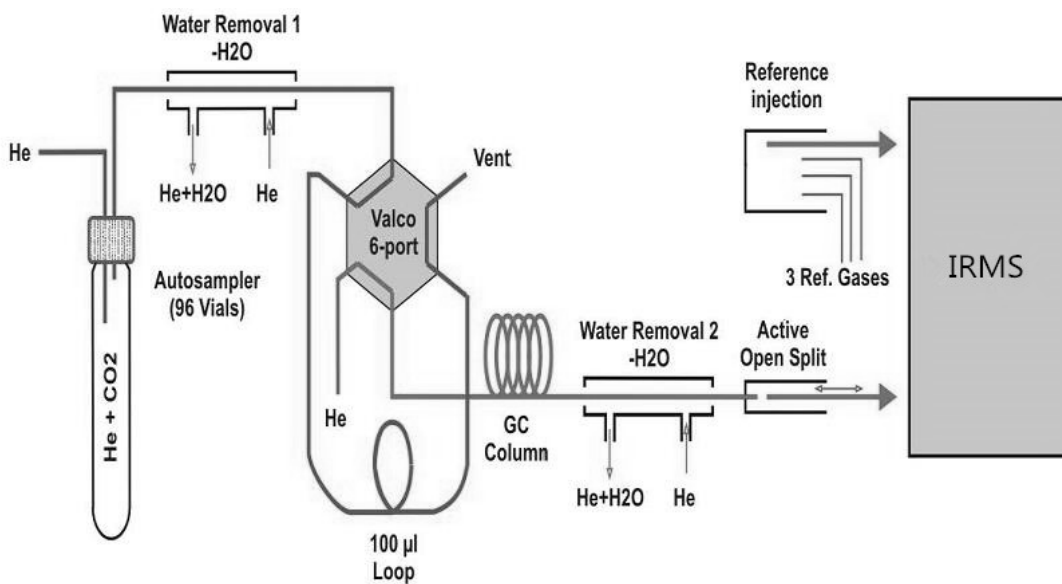


Fig. S2 Schematic diagram of Gasbench II peripheral device interfaced with Delta V Advantage isotope ratio mass spectrometer for $\delta^{13}\text{C}$ analyses of CO_2

Section S1: Calibration of CO₂ gas cylinders

Instrument Description

The Thermo Fisher Scientific Delta V Advantage isotope ratiomass spectrometer (Thermo Scientific, Bremen, Germany) coupled with an online Finnigan Gasbench II peripheral device (Thermo Scientific, Bremen, Germany) was used to measure $\delta^{13}\text{C}$ ratio in CO₂ (Fig. 1). The isotope ratio mass spectrometer and the GasBench were controlled by a personal computer using Isodat 3.0 software (Thermo Scientific, Bremen, Germany).

The GasBench II peripheral device (Fig. 1) consists of a CTC Combi PAL autosampler, a gas sampling system, two maintenance-free water removal systems (Nafion[®] guard trap), a 100 μL loop injection system, an isothermal capillary gas chromatography (GC) column (PoraPlot Q with fused-silica tube, 27.5 m \times 0.32 mm, 10 μm in film thickness; Varian Inc., Palo Alto, CA, USA), an active open split interface, and a reference gas injection system.

Sample preparation

CO₂ gas from the gas cylinders (400 ppm and 52000 ppm) was collected into plastic sampling bags (Flexi Foil PLUS sampling bags). Two samples were prepared from each cylinder. These bags were analyzed for stable carbon isotope in CO₂. Approximately 12 mL exetainers in the aluminium block of the autosampler is kept. The exetainers were subsequently flushed for 300 s on a CTC Combi PAL autosampler, with helium grade 5.0 (99.999% He) at a flow rate of 55 mL/min to remove air contamination. A moderate amount sample air into the exetainers with gastight syringes is extracted for the analysis.

GasBench II-IRMS analytical procedure

The measurement sequence is as follows. Before sample analysis, a peak centering procedure is performed, and three reference gas peaks are measured. Subsequently, the sample gas is introduced four times into the mass spectrometer, by sampling through the standard 100 μL sample loop. The measured carbon isotope ratios are corrected for linearity (drift with sample size) using the relationship between the measured isotopic values of the internal standard and the signal height.

To introduce the sample gas, a specially dual-hole measurement needle (Thermo Scientific) located in the Combi PAL autosampler is used. The measurement needle delivers a He flow (99.999%, 0.4–0.5 mL/min) through the side hole and takes up the sample gas through the needle tip. The He stream gently moves CO₂ and other gas species from the vial into the fused-silica capillary within the needle tip. Then, the sample gas is transferred through a Nafion[®] guard trap to remove the water and through a Valco loop (VICI Valco Instruments Co. Inc., Houston, TX, USA) for injection into a gas chromatography (GC) column.

The loop injection system, equipped with a 100 μL loop, introduces the sample gas into the GC column by a Valco six-port valve, where CO_2 is separated from any other gas species. The GC flow rate is set at 2 mL/min. The temperature of the GC column is kept at 70°C.

The CO_2 eluting from the GC column is then passed through another Nafion® guard trap and introduced into IRMS via the active open split. The reference CO_2 (99.999%) pulse is automatically introduced into IRMS via a reference gas injection system.

The carbon stable isotope compositions are expressed relative to isotope standard reference material (Vienna Pee Dee Belemnite, VPDB), reported as the conventional δ notation rather than as absolute isotope values. The δ notation is defined as $\delta^{13}\text{C}_{\text{sample}} = [(R_{\text{Sample}}/R_{\text{Standard}}) - 1] \times 1000$, where R_{sample} and R_{standard} represent $^{13}\text{C}/^{12}\text{C}$ ratios of the sample and the standard, respectively.

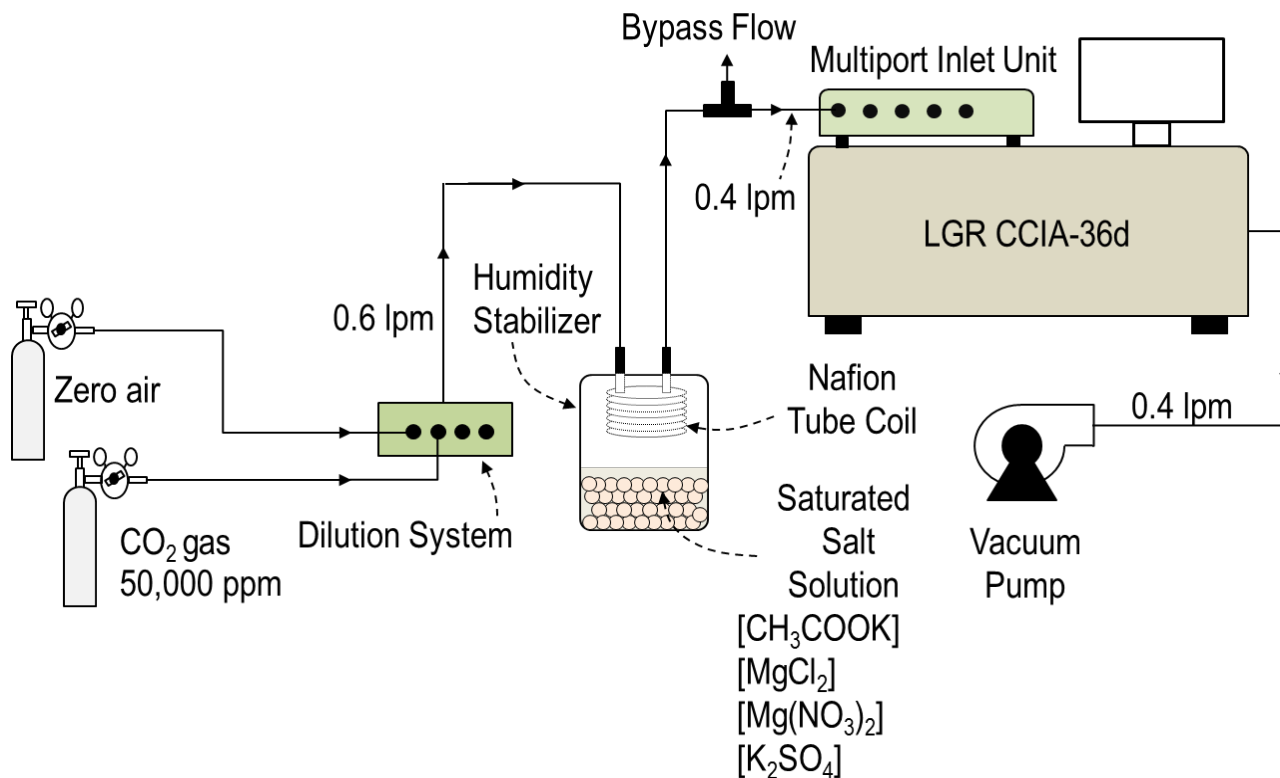


Fig S3: Setup for developing correction equation for drift in CCIA measurement due to varying water vapor concentration using four different salts

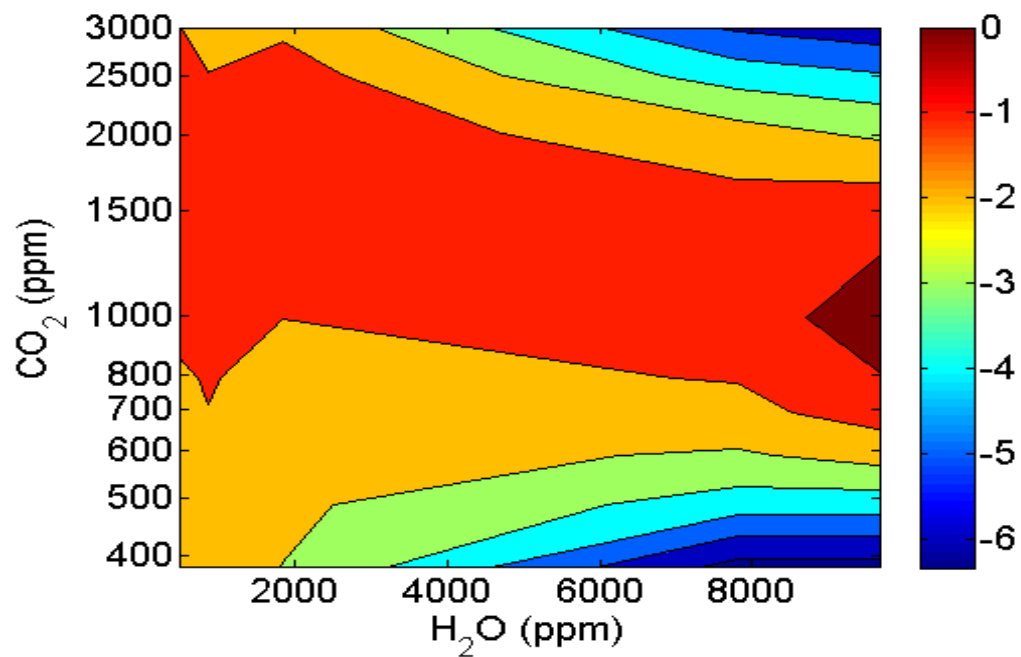


Fig S4: CO₂ and water vapor concentration dependent drift in δ¹³C measurement (measured the humidified value against the dry reference value of the standard gas with different concentration); color bar represents the drift (i.e. $\delta^{13}C_{ccia}(wet) - \delta^{13}C_{ref}(dry)$)

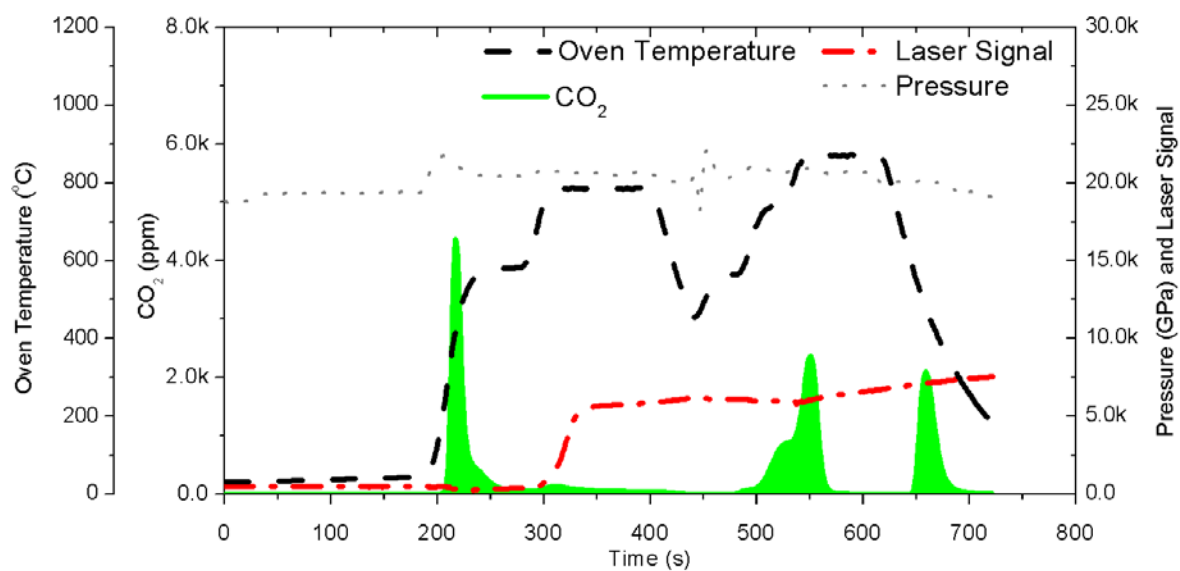


Fig S5-a: A typical output profile of oven temperature, oven pressure, laser signal and CO₂ during the analysis (Thermograph) of diesel sample

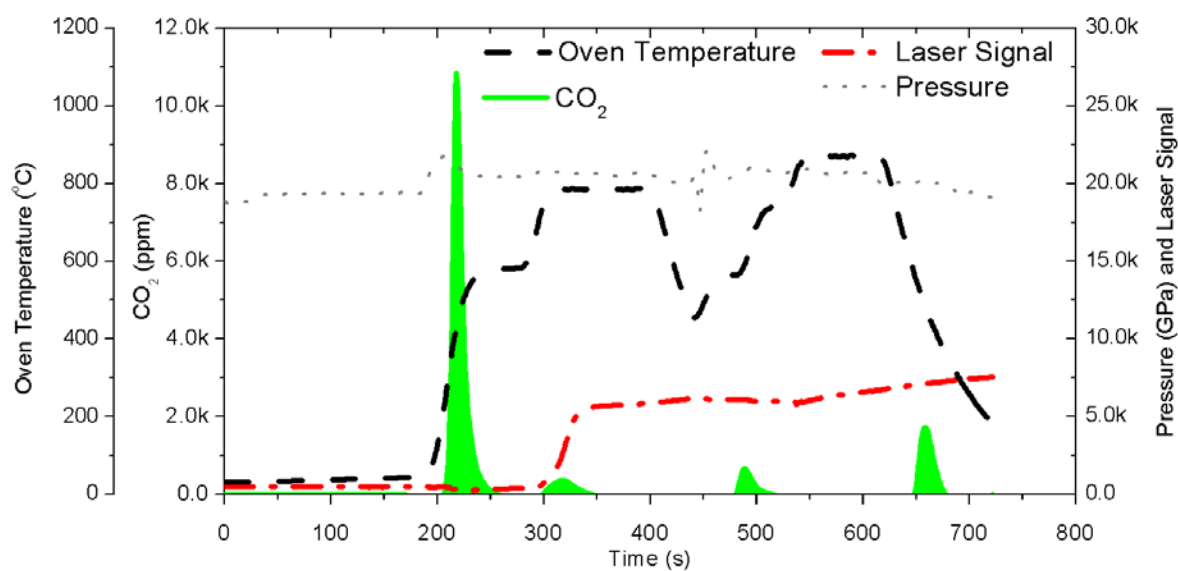


Fig S5-b: A typical output profile of oven temperature, oven pressure, laser signal and CO₂ during the analysis (Thermograph) of ambient sample.

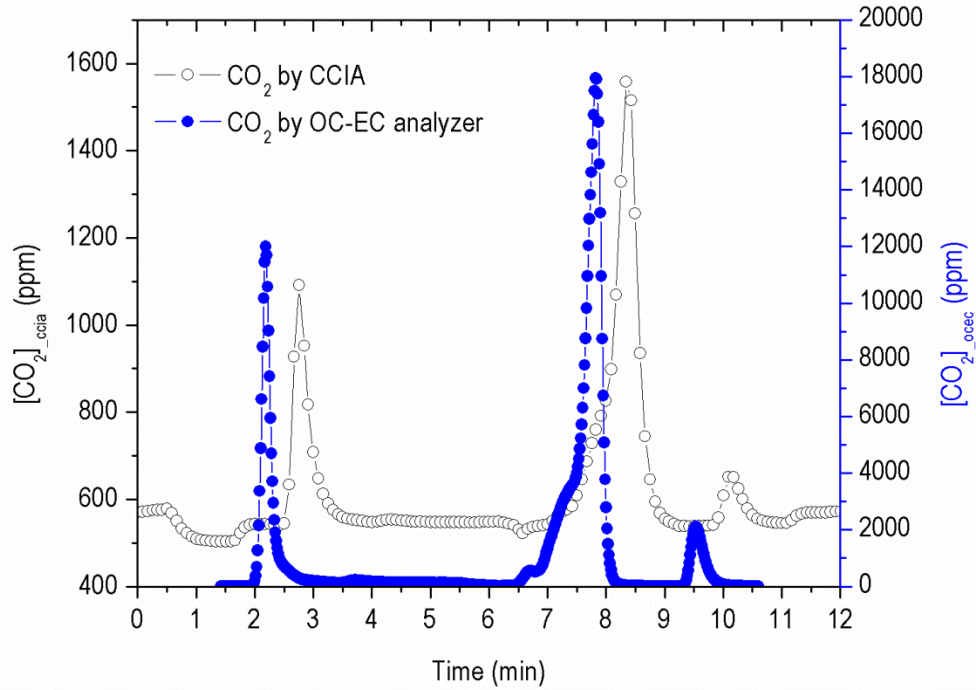


Fig S6: A typical CO₂ profile from OC-EC analyzer and CCIA (single sample). CO₂ from CCIA is 5 s averaged. It shows that signal in NDIR is well captured by OA-ICOS except slight delay and changed peak width and height.

Section S2: Uncertainty in Stable Isotope Ratio Estimation

(I) Estimation of error in stable isotope ratio

The uncertainty in the estimation is the consequence of applied corrections. Following approach has been used to derive error in isotopic ratio estimation. Equation of ratio estimation is as follows:

$$\delta^{13}C_s = \delta^{13}C_b - \frac{S}{C_b} \quad \text{-----(S1)}$$

$$\text{Assume } \delta^{13}C_b = r_s; \delta^{13}C_b = r_b$$

r_s and r_b are the isotopic ratio of sample (/source) and background gas respectively,

Then,

$$r_s = r_b - \frac{S}{C_b}$$

Error in r_s will depend upon error in slope (S) derivation and error in background CO₂ concentration, r_b is constant. Thus,

$$\frac{\partial r_s}{\partial S} = -\frac{1}{C_b}$$

$$\frac{\partial r_s}{\partial C_b} = \frac{S}{C_b^2}$$

$$dr_s = \frac{\partial r_s}{\partial S} dS + \frac{\partial r_s}{\partial C_b} dC_b$$

$$\text{or, } dr_s = \left(\frac{-1}{C_b}\right) dS + \left(\frac{S}{C_b^2}\right) dC_b \text{ ----- (S1')}$$

It can be seen in the table S1 that $S \times dC_b \ll C_b^2$ for the NIST as well as diesel and ambient samples. Thus, second term of equation S2 contribute insignificantly to dr_s . But, the first term does contribute considerably.

$$\text{Thus, } dr_s = \left(\frac{-1}{C_b}\right) dS \quad (S \times dC_b \ll C_b^2)$$

Uncertainty in dependent variable (F) arising from error in multiple variables (x_i), in Einstein notation (i.e. summation over repeated index) is as follows (Ku, H. H., 1966):

$$\sigma_F = \sqrt{\left(\frac{\partial F}{\partial x_i}\right)^2 \sigma_{x_i}^2}$$

Using above equation with $dS = \sigma_S$ and $dr_s = \sigma_{r_s}$, uncertainty in r_s ,

$$\sigma_{r_s} = \sqrt{\left(\frac{-1}{C_b}\right)^2 \sigma_S^2} = \pm \left(\frac{1}{C_b}\right) \sigma_S \text{ ----- (S2)}$$

Equation (S2) has been used to estimate error in isotope ratio measurement of different samples (Table S1). If error in the slope derivation is of the order of C_b , the error in dr_s will be close to 1⁰/₁₀₀. Thus, slope of the keeling curve should be derived precisely ensuring it does not exceed C_b to contain dr_s less than 1⁰/₁₀₀. In the table, it can be seen that dr_s for NIST, diesel and ambient sample are smaller due to better slope derivation ($dS < C_b$) and lesser norm of residuals (indicating better fit to the data).

(II) Working CO₂ range for lower uncertainty in isotope ratio

From equation 5,

$$r_m = r_s + \frac{S}{C_m}$$

$$\text{or, } S = (r_m - r_s)C_m$$

Here, we wanted to qualitatively investigate uncertainty in S due to measurement error in r_m and C_m (from the keeling curve perspective). Thus, r_s is assumed to be constant.

$$\frac{\partial S}{\partial r_m} = C_m$$

$$\frac{\partial S}{\partial C_m} = r_m - r_s$$

$$dS = \frac{\partial S}{\partial r_m} dr_m + \frac{\partial S}{\partial C_m} dC_m$$

$$\text{or, } dS = C_m dr_m + (r_m - r_s) dC_m \text{ --- (S3)}$$

Equation S3 can be used to understand error in the slope. From the Allan variance curve (Fig 3), dr_m and dC_m are ~ 0.4 ‰ and 0.2 ppm, respectively (for 5-s integration).

$$\text{For } C_m > C_b, C_m dr_m \gg (r_m - r_s) dC_m$$

$$\text{Thus, } dS = C_m dr_m \text{ --- (S4)}$$

From equation S4, to contain error in slope (dS) ≤ C_b, operating CO₂ (C_m) range must not exceed dS/ dr_m (~ 1250 ppm) as then error in slope will lead to below 1.0 ‰ error in r_s as explained above. Thus, CCIA is operated in ~400-1300 ppm CO₂ range to control the mentioned error. If sample combustion produces higher concentration than ~1300 ppm, higher values are not included while deriving slope from keeling curve.

Accuracy of the S depends upon the number of data points acquired for keeling curve. Usually, the OC peak of diesel exhaust samples is very narrow and steep which may be attributed to its high carbon content and narrow volatility range of carbon compounds. Such peak produces less

number of data points (Fig S5) as opposed to ambient samples which has compounds of wide volatility range. Although, this shortcoming of the method could be overcome by using different carbon analysis method (other than current NIOSH method) having gradual temperature ramp to allow the peak to spread for acquiring more number of data points.

It has to be noted that the derivation of accurate slope (i.e. better fitting and bringing down dS and norm of residual to minimal possible values and the derived value will define the accuracy of dr_s) is dependent upon mass of carbon as well as the shape of the peak as described earlier. If different OC fractions have separate peaks and good signal in CCIA and if their isotope ratios are different, then they would produce different slope which could be separated. For example, if keeling curve is produced for data including OC and EC peak, slope splits into two for OC and EC each. But, smaller peaks in OC region (smaller fraction e.g Fig S5-b) produces negligible signal to be separated. Thus, only main peak is used to derive the ratio. If smaller peak produces different slope with poor signal, they could be removed as outlier. It is also logical to remove them as they do not contribute substantially to the sample ratio.

Although if the largest OC single peak contain varying isotope ratio then the ratio of sample would be the average value of its component. If variability is large where slope could not be obtained with acceptable accuracy, sample should be neglected. Future investigation would try to develop approach for ratio measurement of OC fractions by using different carbon analysis approach.

Table S1: Error estimation of sample stable isotopic ratio using equation (S2), C_b , S , r_s are background CO₂ concentration, slope of keeling curve and stable sample isotope ratio, respectively. dC_b , σ_s , σ_{r_s} are the errors in respective variables. NIST stands for National Institute of Standards and Technology.

Types of Sample	C_b (ppm)	dC_b (ppm)	S	σ_s	r_s (‰)	σ_{r_s} (‰)	Norms of Residual
<i>NIST standards</i> (5-replicates)	505.41	0.33	13108.21	253.21	-46.74	±0.48	97.83
	508.52	0.25	13670.11	351.86	-47.68	±0.68	106.62
	490.37	0.32	12484.47	255.76	-46.26	±0.50	139.18
	492.34	0.13	12290.75	278.21	-45.76	±0.56	182.28
	490.02	0.32	12533.45	322.31	-46.38	±0.64	5.14
<i>Diesel Exhaust Particles</i> (5-replicates)	495.31	0.13	2071.57	194.87	-24.98	±0.39	31.82
	504.73	0.04	1687.62	227.68	-24.14	±0.45	13.81
	522.68	0.12	2149.86	365.31	-24.91	±0.70	44.68
	525.10	0.18	1834.23	434.82	-24.29	±0.83	60.04
	510.64	0.54	2138.84	299.81	-24.99	±0.59	28.00
<i>Ambient particulate matter</i> (5-replicates)	496.75	0.31	1932.02	196.64	-24.69	±0.39	49.20
	496.15	0.39	1845.16	214.13	-24.52	±0.43	32.45
	500.41	0.23	1811.71	401.86	-24.42	±0.80	78.52
	525.67	0.05	1290.86	338.89	-23.26	±0.64	28.50
	499.64	0.14	1678.30	240.35	-24.16	±0.48	24.71

References:

Ku, H. H., (1966). Notes on the use of propagation of error formulas. *J. Res. Nat. Bur. Stand.* 70C: 263-273