A novel method for carbonate quantification in atmospheric particulate matter

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Supplemental Info

1. *Overview of Calculations*

In calculating the amount of carbonate present in a sample, the concentration of CO_2 released during acidification of a sample must be determined, taking into account changes in the volume and pressure inside of the jar throughout the experiment. At the start of each experiment, the ambient pressure and temperature were measured and monitored throughout the course of the experiment to ensure that no large fluctuations occurred. The ambient pressure and temperature were assumed to be the same as the initial pressure and temperature inside of the incubation jar.

The ideal gas law was first used to determine the moles of gas initially present in the container:

$$n = \frac{p \times V}{R \times T} \qquad \text{(eq. 1A)}$$

where n = moles of gas, p = pressure, V = volume of the container, R = 0.082058 L atm mol^{-1} K^{-1} (ideal gas constant), and T = temperature. To provide an example, the calculations for jar 3 in the experiments performed in Table 1 are detailed below. The jar has a volume of 177.05 mL and contained 0.07622 mg (9.073×10^{-7} mol) of solid $NaHCO_3$ at an ambient pressure of 0.9891 atm and temperature of 294.4 K. The moles of gas initially present in the container are:

$$n = \frac{0.9891\ atm \times 0.17705\ L}{0.082058\ L\ atm\ mol^{-1}K^{-1} \times 294.4\ K} = 0.007249\ mol \quad \text{(eq. 1B)}$$

5 mL of air were then removed from the container using a gas-tight syringe to measure the background CO_2 concentration, resulting in a change in volume of the system:

$$V_1 = V + 0.005\ L \quad \text{(eq. 2A)}$$

where V_1 is the sum of the volume of the container and the volume of the syringe. For this particular jar,

$$V_1 = 0.17705\ L + 0.005\ L = 0.18205\ L \quad \text{(eq. 2B)}$$

A new pressure of the system was calculated based on the change in volume:

$$p_1 = \frac{n \times R \times T}{V_1} \quad \text{(eq. 3A)}$$

Where p_1 is the new system pressure. For the above example,

$$p_1 = \frac{0.007249\ mol \times 0.082058\ L\ atm\ mol^{-1}K^{-1} \times 294.4\ K}{0.18205\ L} = 0.9619\ atm \quad \text{(eq. 3B)}$$

This pressure was then used to calculate the moles of air removed from the container via the 5mL syringe:

$$n_1 = \frac{p_1 \times 0.005\ L}{R \times T} \quad \text{(eq. 4A)}$$

where n_1 = the moles of air in the 5mL syringe. For this example,

$$n_1 = \frac{0.9619\ atm \times 0.005\ L}{0.082058\ L\ atm\ mol^{-1}K^{-1} \times 294.4\ K} = 1.991 \times 10^{-4}\ mol \quad \text{(eq. 4B)}$$

The new moles of air in the incubation jar, n_2, was calculated via subtraction:

$$n_2 = n - n_1 \quad \text{(eq. 5A)}$$

In this system:

$$n_2 = 0.007249\, mol - 1.991 \times 10^{-4}\, mol = 0.007050\, mol \quad \text{(eq. 5B)}$$

A new pressure inside of the jar, p_2, was then calculated:

$$p_2 = \frac{n_2 \times R \times T}{V} \quad \text{(eq. 6A)}$$

$$p_2 = \frac{0.007050\, mol \times 0.082058\, L\, atm\, mol^{-1} K^{-1} \times 294.4\, K}{0.17705\, L} = 0.9619\, atm \quad \text{(eq. 6B)}$$

The background CO_2 concentration, $[CO_2]_b$, was measured in this jar to be 500 ppmv. 2.2 mL of 1M HCl was then added to the jar, resulting in a new volume container, V_3:

$$V_3 = V - V_{HCl} \quad \text{(eq. 7A)}$$

$$V_3 = 0.17705\, L - 0.0022\, L = 0.17485\, L \quad \text{(eq. 7B)}$$

After sufficient time was provided for the acid to react with the carbonate sample, 5 mL of air were again removed for CO_2 measurements, resulting in V_4, the volume of the container containing acid and with the 5 mL syringe in place:

$$V_4 = V_3 + 0.005\, L \quad \text{(eq. 8A)}$$

$$V_4 = 0.17485\, L + 0.005\, L = 0.17985\, L \quad \text{(eq. 8B)}$$

A new pressure inside of the jar, p_3, was calculated:

$$p_3 = \frac{n_2 \times R \times T}{V_4} \quad \text{(eq. 9A)}$$

$$p_3 = \frac{0.007050\, mol \times 0.082058\, L\, atm\, mol^{-1} K^{-1} \times 294.4\, K}{0.17985\, L} = 0.9470\, atm \quad \text{(eq. 9B)}$$

The moles of air removed by the 5 mL syringe during sampling, n_3, were calculated,

$$n_3 = \frac{p_3 \times 0.005\, L}{R \times T} \quad \text{(eq. 10A)}$$

$$n_3 = \frac{0.9470\, atm \times 0.005\, L}{0.082058\, L\, atm\, mol^{-1} K^{-1} \times 294.4\, K} = 1.960 \times 10^{-4}\, mol \quad \text{(eq. 10B)}$$

followed by the moles of air remining in the jar, n_4,

$$n_4 = n_2 - n_3 \quad \text{(eq. 11A)}$$

$$n_4 = 0.007050\, mol - 1.960 \times 10^{-4}\, mol = 0.006854\, mol \quad \text{(eq. 11B)}$$

assuming that the moles of CO_2 gas formed would have a minimal contribution to the total moles n_2 or n_4. The new pressure in the container, p_4, was then determined:

$$p_4 = \frac{n_4 \times R \times T}{V_3} \quad \text{(eq. 12A)}$$

$$p_4 = \frac{0.006854\ mol \times 0.082058\ L\ atm\ mol^{-1} K^{-1} \times 294.4\ K}{0.17485\ L} = 0.9470\ atm \quad \text{(eq. 12B)}$$

The concentration of CO_2 gas in the system, $[CO_2]_1$, was measured as 596 ppmv. The concentration of CO_2 that formed in the reaction $[CO_2]_f$, was calculated,

$$[CO_2]_f = [CO_2]_1 - [CO_2]_b \quad \text{(eq. 13A)}$$

$$[CO_2]_f = 596\ ppmv - 500\ ppmv = 96\ ppmv \quad \text{(eq. 13B)}$$

and the moles of CO_2 formed were determined:

$$n_{CO_2} = \frac{[CO_2]_f \times 10^{-6} \times p_3 \times V_4}{R \times T} \quad \text{(eq. 14A)}$$

$$n_{CO_2} = \frac{96\ ppmv \times 10^{-6} \times 0.9470\ atm \times 0.17985\ L}{0.082058\ L\ atm\ mol^{-1} K^{-1} \times 294.4\ K} = 6.769 \times 10^{-7}\ mol \quad \text{(eq. 14B)}$$

If subsequent measurements of $[CO_2]_f$ were made, the moles of formed CO_2 that were removed by the syringe were calculated, and this value was added to the next calculation of n_{CO2} to account for sampling loss:

$$n_{CO_2} sampled = \frac{0.005\ L}{V_4} \times n_{CO_2} \quad \text{(eq. 15A)}$$

$$n_{CO_2} sampled = \frac{0.005\ L}{0.17985\ L} \times 6.768 \times 10^{-7}\ mol = 1.882 \times 10^{-8}\ mol$$

(eq. 15B)

Table S1, ***Experiments performed on three containers at 5, 15, and 25 minutes, and 4 hours after HCl addition, to determine a suitable incubation time.***

							5 Minute Incubation		
Incubation Jar Number	Ambient Pressure (atm)	Ambient Temperature (K)	Amount of $NaHCO_3$ ($\times10^{-7}$ mol)	Volume of Container (L)	Background CO_2 Concentration (ppmv)	Volume 1M HCl added (L)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times10^{-7}$ mol)	Relative Error (%)
C	0.9891	294.5	3.70	0.1771	698	0.003	729	2.185	-40.94
J	0.9891	294.5	3.44	0.1776	562	0.003	592	2.122	-38.24
K	0.9891	294.5	4.23	0.1773	522	0.003	579	4.024	-4.82

	15 Minute Incubation			25 Minute Incubation			4 Hour Incubation		
Incubation Jar Number	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times10^{-7}$ mol)	Relative Error (%)
C	723	1.774	-52.05	719	1.508	-59.25	630	-4.255	-215.00
J	590	1.984	-42.24	587	1.784	-48.08	577	1.134	-66.99
K	577	3.887	-8.06	575	3.754	-11.22	553	2.327	-44.97

Table S2 ***Experiments performed on three containers at 15, 20, and 25 minutes, and 3.5 hours after HCl addition, to determine a suitable incubation time.***

							15 Minute Incubation		
Incubation Jar Number	Ambient Pressure (atm)	Ambient Temperature (K)	Amount of $NaHCO_3$ ($\times 10^{-7}$ mol)	Volume of Container (L)	Background CO_2 Concentration (ppmv)	Volume 1M HCl added (L)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)
C	0.9933	294.5	5.02	0.1771	453	0.003	512	4.176	-16.82
J	0.9933	294.5	4.40	0.1776	461	0.003	509	3.409	-22.59
K	0.9933	294.5	4.49	0.1773	468	0.003	519	3.616	-19.50

	20 Minute Incubation			25 Minute Incubation			3.5 Hour Incubation		
Incubation Jar Number	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)
C	509	3.970	-20.93	506	3.769	-24.93	496	3.119	-37.88
J	507	3.271	-25.73	505	3.137	-28.78	508	3.333	-24.33
K	515	3.340	-25.64	514	3.273	-27.13	504	2.622	-41.63

Table S3 ***Experiments performed on three containers to determine a suitable incubation time. The first measurement was taken 20 minutes after HCl addition, and subsequent measurements were taken every 30 minutes.***

							20 Minute Incubation		
Incubation Jar Number	Ambient Pressure (atm)	Ambient Temperature (K)	Amount of $NaHCO_3$ ($\times 10^{-7}$ mol)	Volume of Container (L)	Background CO_2 Concentration (ppmv)	Volume 1M HCl added (L)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)
C	0.9924	294.4	4.05	0.1771	458	0.003	511	3.749	-7.46
J	0.9924	294.4	3.52	0.1776	457	0.003	500	3.052	-13.37
K	0.9924	294.4	3.61	0.1773	459	0.003	505	3.260	-9.74

	50 Minute Incubation			80 Minute Incubation			110 Minute Incubation		
Incubation Jar Number	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)
C	507	3.474	-14.25	502	3.140	-22.50	499	2.945	-27.31
J	499	2.983	-15.33	497	2.849	-19.14	495	2.719	-22.84
K	503	3.122	-13.56	499	2.854	-20.97	497	2.724	-24.58

	140 Minute Incubation			170 Minute Incubation		
Incubation Jar Number	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)	CO_2 Pressure (ppmv)	Moles CO_2 Formed ($\times 10^{-7}$ mol)	Relative Error (%)
C	495	2.693	-33.55	491	2.447	-39.61
J	494	2.655	-24.64	492	2.532	-28.14
K	494	2.534	-29.83	492	2.411	-33.24