

Quantification of carbonate carbon in aerosol filter samples using a modified thermal/optical carbon analyzer (M-TOCA)

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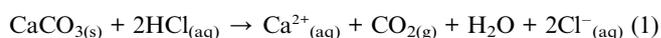
Measurement of carbon dioxide (CO₂) gas evolved from acidification is a method to quantify carbonate carbon (CC) in aerosols collected on quartz fiber-filters. This paper describes the installation of an add-on device in a DRI Model 2001 Thermal Optical reflectance (TOR)/Thermal Optical Transmittance (TOT) Carbon Analyzer (M-TOCA) to facilitate a direct CC measurement. In each run, a maximum of 20 filter punches (each of 0.5 cm²) were acidified with 1 mL of 20% v/v phosphoric (v) acid in a vial under a 100% helium gas environment. The CO₂ evolved was reduced to methane (CH₄) and detected by a flame ionization detector (FID). The optimum reaction kinetics were obtained under an operational temperature of 40 °C and ultrasonic agitation. Method precisions were ±3.5% on average for carbonate standards ranging from 3.0 to 60.0 µg and ±3.8% on average for ambient samples in masses ranging from 0.30 to 56.0 µg respectively. Method accuracy was on average 91.9%, ranging from 81.4 to 102.1%. Minimum detection limit (MDL) of the M-TOCA method was 0.048 µg cm⁻², corresponding to an ambient concentration of 0.098 µg m⁻³ for a sampled volume of air of 7.2 m³. The MDL is >22 times lower than the value obtained using the novel method with a regular TOCA. Comparison studies on standards and ambient samples have demonstrated that the two methods do not yield systematic differences in concentrations of the carbonate. The lower MDL value provided by the M-TOCA allows a simple, precise and accurate measurement for ambient samples having a low CC concentration.

1. Introduction

Thermal evolved-gas analysis has been widely used for quantification of carbonaceous particulate matter (PM), organic carbon (OC) and elemental carbon (EC) in atmospheric aerosols.^{1–6} Carbonate carbon (CC) is another primary carbonaceous species

present in natural soil and building or demolition dust. It exists in metal-associated forms [*e.g.*, calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃)] in the atmosphere.⁷ It mainly presents in aerosol coarse mode (PM₁₀–PM_{2.5}), but its contribution in respirable fine mode [*i.e.*, (PM_{2.5}), PM with aerodynamic diameter less than or equal to 2.5 micrometers] is not negligible, especially in areas influenced by specific meteorological conditions such as soil dust outbreaks.^{7,8} Typical concentrations of CC in PM_{2.5} fraction range from 0.42–15.8 µg m⁻³.^{1,7–12} However, depending on the thermal protocol, CC is measured either as OC or EC in thermal evolved-gas analysis.^{13,14} Birch and Cary¹⁵ recommended that the interference of CC can be avoided by removing it from the filter samples by acidification with acidic fumes prior to thermal or thermal-optical analysis.

A sensitive quantification of CC in carbonaceous PM is thus critical. For the direct measurement, a filter punch is acidified [*e.g.*, with hydrochloric acid (HCl)] and carbonate (*e.g.*, CaCO₃) reacts as:



The evolved carbon dioxide (CO₂) is subsequently measured in a carbon analyzer^{1,5,7,15–18} and CC is calculated. Pio *et al.*¹⁹ alternatively used phosphoric (v) acid (H₃PO₄) and the released

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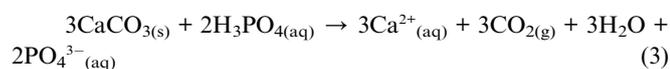
CO₂ was measured by a non-dispersive infra-red spectrophotometer (NDIR). Ionic-balance is an indirect approach to estimate the carbonate concentration.¹⁷ Cations [*i.e.*, sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), Ca²⁺, and Mg²⁺] and anions [*i.e.*, fluoride (F⁻), chloride (Cl⁻), nitrate (NO₃²⁻), and sulfate (SO₄²⁻)] in the filter extracts are quantified using ion chromatography (IC) with conductivity detection. The equivalent concentration of carbonate ($E_{\text{carbonate}}$) is then calculated as

$$E_{\text{carbonate}} = E_{\text{cations}} - E_{\text{anions}} \quad (2)$$

where E_{cations} and E_{anions} are the summations of equivalent concentrations of cations and anions, respectively. However, the presence of other abundant ions (*e.g.*, oxalate) may introduce significant uncertainties in the ionic balance calculation.

The thermal/optical carbon analyzer (TOCA) measures OC and EC fractions based on the preferential oxidation at different temperatures.²⁰ A small punch (*i.e.*, 0.5 cm²) taken from the quartz-fiber filter is heated stepwise in the analyzer in different environments [*i.e.*, pure helium (He) for OC and 2% oxygen in He for EC], where the carbonaceous material is volatilized and converted to CO₂ by a heated manganese dioxide (MnO₂) converter at 912 °C. The CO₂ is then reduced to methane (CH₄) by passing through a hydrogen-enriched nickel methanator. The CH₄ equivalent to the carbon content is finally quantified with a flame ionization detector (FID). The contribution of pyrolyzed OC to EC is accounted for by continuous monitoring of the reflectance and/or transmittance signals.^{21,22} CC is determined by direct measurement of the CO₂ evolved upon the acidification of the sample punch prior to the regular OC/EC analysis in the carbon analyzer.^{1,20} However, only a small filter area can be analyzed in each run, resulting in a high method detection limit. Besides, the acids evolved as gases are permanently reducing the catalytic MnO₂ to manganese(II) in the oxidizer at high temperature, which decreases oxidation efficiency. The idea of subsequent quantification (acidification of CC followed by thermal/optical analysis of OC/EC) on the same filter punch is questionable as well. The acids and the dissociated anions (*e.g.*, Cl⁻ ion from HCl) can lead to intense charring phenomena in the aerosol samples during thermal/optical analysis in an oxidizing atmosphere.¹⁷

In this paper we demonstrate simple modification on a TOCA (M-TOCA) to conduct a single CC measurement of ambient aerosol samples collected on quartz fiber filters. An acidification vial is installed to the instrument which can be flushed with He carrier gas. Acidification was conducted with H₃PO₄ following eqn (3):



and by the use of ultrasonic agitation.

2. Experimental

2.1. Chemicals

Calcium carbonate (CaCO₃) (99+%) was purchased from Acros Organics (Geel, Belgium). Sodium carbonate (NaCO₃) (99.5%) was purchased from Riedel-de Haën (Hanover, Germany). Phosphoric acid (20% v/v) and hydrochloric acid (35% v/v) were

purchased from BDH Prolabo (Dorset, United Kingdom). Nanopure infinity water was obtained from Barnstead Ultrapure Water System (Model D14031, 18 mΩ, Dubuque, IA, USA) which was used for preparation of standard solutions and dilution of acids.

2.2. Instrumental set-up

An add-on device was connected to the regular DRI Model 2001 TOCA (Atmoslytic, Inc., Calabasas, CA, USA). A schematic diagram of the instrumental set-up is shown in Fig. 1. The acidification is performed in a capped glass vial (10 mL in volume), which is positioned in a temperature-controlled ultrasonication water bath. Three small holes were drilled in the cap that fit into the insertions of Teflon tubes (1/16" o.d.), including (i) gas inlet, (ii) acid injection port and (iii) gas outlet, respectively. A manual stainless steel switch was installed at the end of the oxidizer and switched to a "closed" position when the carbonate analysis is performed. This directs a pure He gas flow to pass through the vial at a rate of 50 mL min⁻¹. In the acid injection port, a Teflon inlet was equipped on the top of the cap and was only opened to inject the acid. The gas outlet tube was connected to the methanator of the TOCA.

2.3. Sample analysis

A maximum of 20 filter punches (each of 0.5 cm²) from a parent sample are placed into an empty acidification vial attached to the instrument. Three filter punches were used for the analysis of the ambient samples in each run in this study. The vial was kept in the ultra-sonication water bath at 40 °C for at least 90 seconds. This allows the filter to attain the desired environment and purges any CO₂ out from the vial. One milliliter of 20% v/v H₃PO₄ is injected into the vial through the acid injection port. The amount is theoretically sufficient to neutralize 124 μg of CC. The acid injection port is then closed to avoid any loss of CO₂ evolved. Once the volume of acid is entirely injected, the sonication starts and the computer program begins to acquire the data from the carbonate analytical protocol. The CO₂ evolved from the acidification is entrained into the carrier gas stream, reduced to CH₄ by a hydrogen-enriched nickel catalyst in the methanator, and finally detected by the FID. An aliquot of 1 mL of calibration gas (5% CH₄ by volume in He) is automatically introduced into the line once the FID signal returns to its baseline. The integrated peak area is divided by the calibration peak area and multiplied by an instrument-specific calibration slope and a y-intercept to obtain μg C per sample. After each run, the used filter punches and the acid solution are discarded and a new vial is installed for the subsequent analysis.

2.4. Calibration and minimum detection limit (MDL)

A five-point calibration curve was established by plotting the ratio of the CH₄ peak areas between sample and calibration gas from the FID *versus* micrograms of the carbonate standards. Two carbonate standards were used to demonstrate the feasibility of analysis of liquid- and solid-phase samples. For the liquid-phase calibrations, Na₂CO₃ was weighed using an electronic micro-balance (Model A200 S-D1B, Sartorius, Göttingen, Germany) and dissolved in a volumetric flask with Nanopure

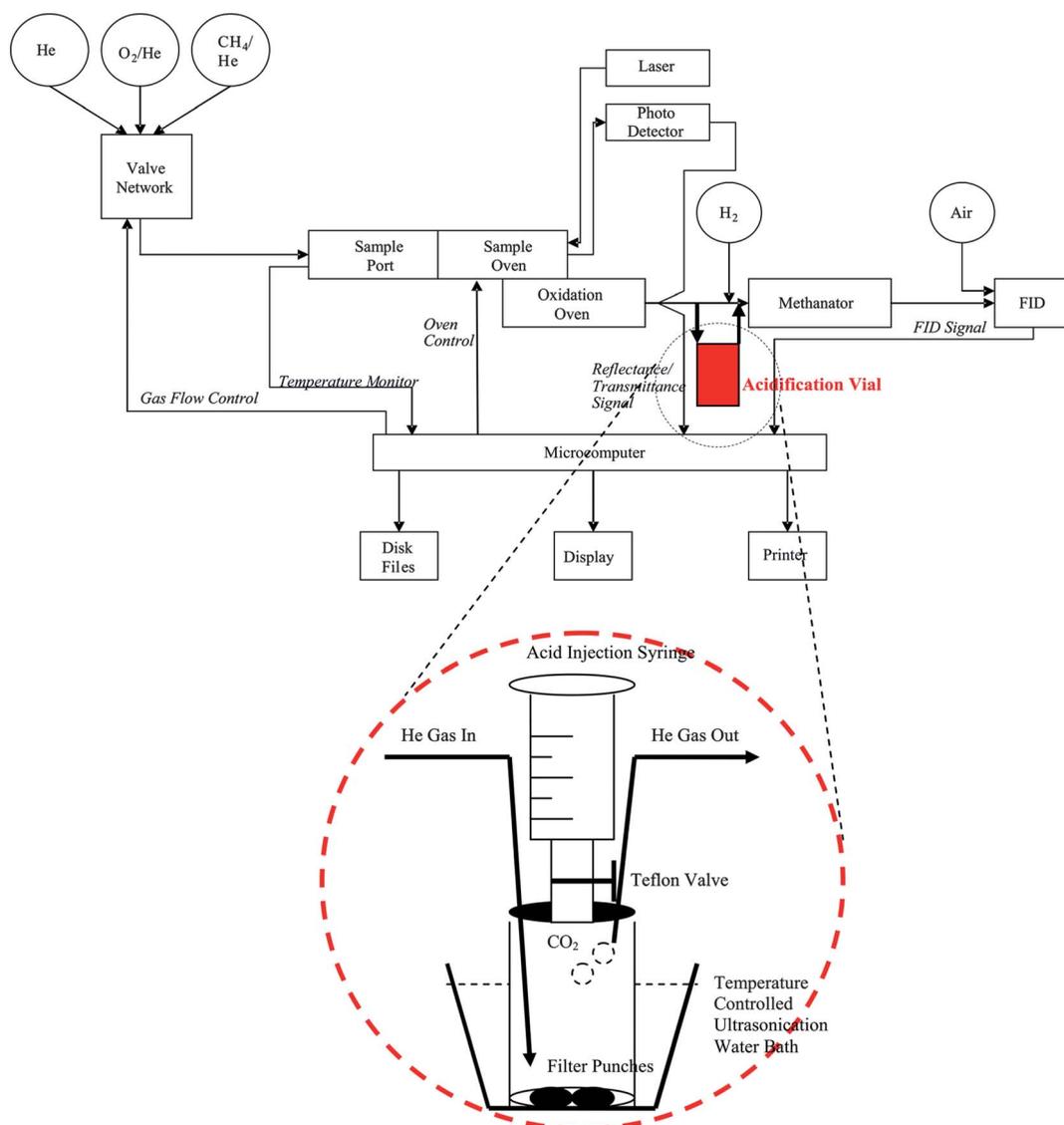


Fig. 1 Schematic diagram of a M-TOCA for the direct carbonate measurement.

infinity water. A range of 0.4–1.0 mL of known concentration standard solution was added to the acidification vial. A solid-phase calibration curve was established by analysis of CaCO_3 deposited on filters, as it is not possible to dissolve it in water due to its low solubility product ($K_{\text{sp}} = 4.8 \times 10^{-9}$).²⁷ The CaCO_3 standards were weighed on prebaked (900 °C, 3 h) filter punches using the microbalance and cautiously squashed on the filter surface using a stainless steel flattened rod. Careful handling is required to avoid any loss of standard particles from the punch. The analytical procedures for the calibration standards were the same as for the filter samples. The method minimum detection limit (MDL) is defined as the amount of carbonate that generates an analytical signal equal to the mean of multiple blank measurements plus three times their standard deviation.^{23,24}

2.5. A novel method for determination of carbonate

The calibration standards and the ambient samples were also analyzed using the novel CC measurement method described by

Chow and Watson (2002).¹ The method was applied on the regular TOCA. An aliquot of the quartz fiber-filter was placed into a quartz boat in the sample holder (at the “calibration” position) in a 100% He gas stream of 50 mL min^{-1} for 90 seconds. A microsyringe (Alltech, Deerfield, IL, USA) was used to deposit 20 μL of 0.4 M HCl onto the filter through a septum cap. The amount of acid is sufficient to neutralize 96 μg of CC on the filter. The quartz fiber-filter acts as a wick to distribute the acid evenly throughout the filter and its particle deposit. Evolved CO_2 gases were reduced to CH_4 , which was detected by FID.

2.6. Sampling collection

A batch of air samples was collected at Tongyu station (44°25'N, 122°52'E, 184 m above sea level), which is located at Xinhua downtown, Tongyu County, Jilin Province, representing a semi-arid area in Northeastern China.^{8,25,26} Meteorological data show the mean annual precipitation is 404 mm in Tongyu. There are no major industrial activities surrounding the sampling location and

it is situated in grassland, about 3 m above ground level. Another batch of air samples was collected at Chai Wan, situated in an urban residential area in Hong Kong. Small scale road construction work was being carried out in this district at the time of sampling.

A Federal Reference Material (frm) Omni Ambient Air Sampler (BGI Incorporated, Waltham, MA, USA) was used to collect PM_{2.5} sampled at a flow rate of 5 L min⁻¹.⁸ The sampler was equipped with a solar power battery to avoid power failure. Daily sampling was conducted from 08:00 a.m. to 08:00 a.m. local time next day from 22nd April 2006 to 8th June 2006. The total sampled volume per sample is 7.2 m³. A total of 19 PM_{2.5} samples were collected on preheated (900 °C for 3 h) 47 mm quartz microfibre filters (QM/A, Whatman, Clifton, NJ, USA). Particle loaded filters were properly stored at -4 °C to avoid microbial degradation of organics and evaporation of semi volatile components. One field blank filter was collected every week to subtract positive artifacts due to adsorption of gas-phase organic components onto the filter during and/or after sampling.

3. Results and discussion

3.1. Acidification efficiency

The acidification of carbonate must occur immediately once the acid has been added to a sample. The reaction kinetics are controlled by chemical and physical parameters such as the amount and strength of the acid and the operational temperature. A series of experiments were performed to define optimum conditions for the carbonate analysis. First, the amount of acid must be sufficient for the acidification. We have examined the acidification efficiency of H₃PO₄ by reaction with the aqueous NaCO₃ solution and the CaCO₃ deposit punches. With 1 mL of 20% v/v H₃PO₄ containing 10.3 μmol of H⁺, the acidification is complete within five minutes, evidenced by the experimental carbon value being equal to the theoretical carbon value. The greatest amount of the carbonate standard (313 μg, equivalent to 5.2 μmol of carbonate) was examined while the molar ratio of carbonate to acid is 1 : 2. This loading corresponds to a CC mass concentration of 21.3 μg cm⁻², which is at least twice the value in the ambient samples collected in Tongyu, China during the dust storm period.⁸ Fig. 2 demonstrates the acidification efficiency with a variety of acid concentrations. For a heavy CC loading sample (313 μg in mass), no further increase in carbon value was seen when the acidification time reached 250 s using 20% v/v H₃PO₄. It took 350 s to complete the acidification when the acid concentration was reduced by half. The impact of acidity on the acidification efficiency was not obvious when a lower CC loading sample (32.5 μg in mass) was analyzed. A stronger acid is not suitable because it can corrode the stainless steel tubing, valves, and the FID in the carbon analyzer. In addition, the volume of acid (1 mL) is enough to moisten a maximum of 20 pieces of filter punches (each 0.5 cm²) in the acidification vial. The injection of a larger volume of acid may decelerate the rate of CO₂ evolved from the solution.

The acidification temperature was optimized. Two aliquots of the PM_{2.5} aerosol-loaded filter punches were analyzed at 20 °C (room temperature) and 40 °C, respectively. The PM_{2.5} mass on

the filter is 256 μg cm⁻². Fig. 3 compares their thermograms. A few moderate signal peaks were observed in the thermogram for the sample analyzed at 40 °C (signal a). An experimental CC value of 9.3 μg was reported. For the samples analyzed at 20 °C, one large signal together with a few smaller signal peaks were seen in the thermogram (signal b). An experimental CC value of 4.4 μg C was reported which is >50% lower than the value obtained in the analysis of the aliquot sample at 40 °C. The same phenomenon was observed in the analysis of the calibration samples. The recoveries ranged only from 79% to 88%, through comparing with the real values, for the samples analyzed at 20 °C. No further increase of the experimental carbon value was reported for the aliquot aerosol samples analyzed at 60 °C. An excessively high operational temperature can result in evaporation of any volatile organic compounds from the samples that interfere with the baseline of FID.

The acidification of the aerosol samples is generally slower than that of the calibration samples. A prolonged time is required for the hydrogen ion to penetrate into the PM layers and for the CO₂ gas to evolve from the filter matrix. Vibration can assist the acids to diffuse speedily into the filter punches. Ultra-sonication was thus applied to guarantee a constant and powerful mixing between each run.

3.2. Calibration and detection limits

Table 1 lists the regression slopes, *y*-intercepts, and coefficients of determination (*R*²) for the carbon calibrations of liquid- and solid-phase CC and sucrose solution. Standard samples containing 2.96–62.6 μg C per sample were analyzed. The regression slopes obtained in the three calibrations were consistent (with a deviation <1.6%), with an *R*² value close to 1. The intercepts of the regressions are negligible below +0.07. This recovery test demonstrates that CC decomposes almost completely during the acidification steps. A recovery of >95% was found for these high CC content levels.

The MDL of the M-TOCA method is obtained as the minimum amount of the CC that generates the minimum detectable analytical signal *S*_m. *S*_m is taken as the sum of mean blank signal *S*_{b1} plus three times the standard deviation of the blank signal *σ*_{b1}, *i.e.*, *S*_m = *S*_{b1} + 3*σ*_{b1}.^{19,20} The MDL is calculated as (*S*_m - *b*)/*k*, where *b* and *k* are the calibration curve intercept and slope respectively. A total of 20 blanks were analyzed. The CC concentrations of the blank filter punches ranged from 0.025 to 0.050 μg cm⁻², with an average of 0.030 μg cm⁻². The standard deviation of the blank was 0.006 μg cm⁻². The MDL is thus calculated as 0.048 μg C cm⁻² and can be translated to 0.098 μg m⁻³ for a sampling volume of 7.2 m³ when a maximum of 20 filter punches (each of 0.5 cm²) are used in each analysis. If the sampled air volume or flow is increased, the MDLs would be proportionally lower. Pio *et al.*¹⁹ adopted a similar set-up for measurement of carbonate collected on filter samples. The acidification was also performed using 20% v/v H₃PO₄ and the released CO₂ was measured by a NDIR. The MDL was 1 μg cm⁻² when a filter portion of 1.2 cm² is used in each analysis. The values are >20 times higher than the MDLs measured using the M-TOCA.

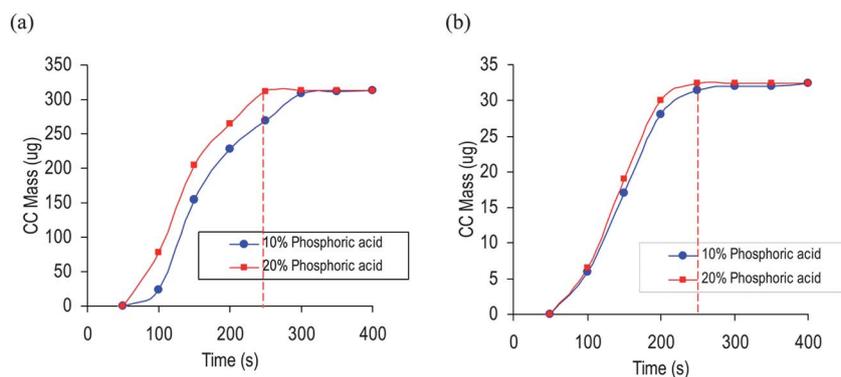


Fig. 2 Efficiency of acidification with a variety of acid concentrations for (a) a heavy CC loading sample (313 μg) and (b) a lower CC loading sample (32.5 μg).

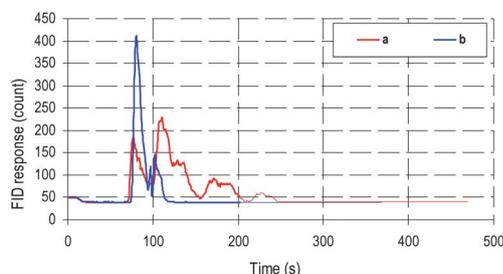


Fig. 3 Two aliquots of aerosol loaded filter punches were analyzed at (a) 40 $^{\circ}\text{C}$ and (b) 20 $^{\circ}\text{C}$, respectively, with ultra-sonication.

3.3. Method precision and accuracy

Precision was measured by analysis of standard multiple samples, including the aqueous Na_2CO_3 solutions and the CaCO_3 deposit punches respectively (Table 2). The precisions for the liquid standards were $\pm 3.2\%$ on average for masses ranging from 3.0 to 36.0 μg , while the precisions for the solid samples were $\pm 4.0\%$ on average for CC masses ranging from 20.0 to 60.0 μg . The sample precisions were measured by the multiple analyses of eight ambient samples. The precisions were $\pm 5.7\%$ on average for masses ranging from 0.30 to 56.0 μg . Our precisions are much better than the values ($\pm 15\%$) obtained using HCl/TOCA with different thermal protocols⁷ and consistent with the values ($\pm 9\%$) obtained using the H_3PO_4 /NDIR method.¹⁹ There is a lack of any certified standard or reference material for carbonate on the market. Method accuracy was determined by measuring the recovery of 10.0 μg of CC in standard-spiked ambient samples. The method accuracy was 91.9% on average,

ranging from 81.4 to 102.1%. The method precisions and accuracies both reveal the feasibility of the M-TOCA for the determination of carbonate.

3.4. Method comparison

The M-TOCA was validated with the carbonate measurement method described by Chow and Watson.¹ When analyzing 20 blanks, the method MDL for CC using the novel approach is 1.10 $\mu\text{g cm}^{-2}$, which can be converted to 2.30 $\mu\text{g m}^{-3}$ for a sampling volume of 7.2 m^3 . The values are >22 times higher than the method MDLs measured using the M-TOCA. Twenty calibration punches and 35 ambient aerosol filter samples (19 ambient samples collected at Tongyu, China and 16 ambient samples collected at Chai Wan, Hong Kong) were analyzed in this comparison study. The CC concentrations in nine ambient samples are below the method MDL using Chow and Watson's approach but are within the determination range of the M-TOCA method. These samples were thus not used in the comparison. Fig. 4 plots the concentrations of carbonate measured using both methods. The slopes for the carbonate standards and the aerosol samples were 1.01 and 1.31, respectively, generally giving comparable concentrations. The difference in individual pairs of measurement does not exceed 32%. Higher values were usually seen for heavy loaded ambient samples measured using the M-TOCA method. This suggests that the acidification was incomplete for these samples measured using Chow and Watson's method.

Table 3 compares the two analytical methods. As well as showing higher method MDLs, there are a few additional disadvantages of using the method published by Chow and Watson.¹ First of all, uneven distribution or slow diffusion of the

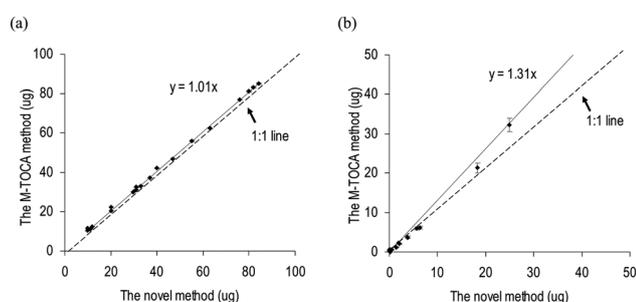
Table 1 Linear regression parameters for calibration curves

Standard	Slope ^a	y-Intercept (peak count ratio) ^a	Coefficients of determination (R^2) ^a	Mass loading range ($\mu\text{g C}$)
<i>Carbonate calibration</i>				
Na_2CO_3 solution	22.5	0.07	0.998	2.96–36.0
CaCO_3 deposit filter	22.2	0.06	0.996	3.00–62.6
<i>Carbon calibration</i>				
Sucrose	22.4	0.04	0.999	9.54–38.2

^a Calibration values are plotted as ratio of the integrated sample peak counts to the calibration peak counts vs. actual μg carbon.

Table 2 Method precisions measured with liquid standards (aqueous sodium carbonate solutions) and solid standards (calcium carbonate deposit punches)

CC mass (μg)	Standard concentration ($\mu\text{g mL}^{-3}$)	Injection volume (mL)	Number of observations N	Precision
<i>Aqueous sodium carbonate solutions</i>				
3.0	3.6	0.5	8	$\pm 5.2\%$
6.7	13.4	0.5	4	$\pm 3.2\%$
13.4	13.4	1.0	3	$\pm 3.0\%$
36.0	72.0	0.5	8	$\pm 1.3\%$
CC mass (μg)	Number of observation n		Precision	
<i>Calcium carbonate deposit filters</i>				
20.0	4		$\pm 6.1\%$	
40.0	6		$\pm 3.4\%$	
60.0	5		$\pm 2.5\%$	

**Fig. 4** Comparisons of the CC masses in (a) carbonate standard and (b) the ambient samples collected in Tongyu, China and Chai Wan, Hong Kong measured by the M-TOCA method and the method described in Chow and Watson¹ respectively.

acid may cause delayed or incomplete acidification. For heavy loaded filter samples, the PM may contain a large quantity of hygroscopic substances which inhibit the acid droplet to spread out on the entire punch. Besides, chloride from the acid may interact with quartz, as with other ions like sodium and potassium, that frost the quartz boat surface when the sample is heated for OC and EC determination at >650 °C after the acid treatment. Lastly, the acids evaporating into the gas stream can permanently reduce the catalytic MnO_2 to manganese(II) in the oxidizer at high temperatures, which decreases the oxidation

efficiency in the regular thermal analysis. The replacement of the instrumental parts and the catalyst not only increases the maintenance cost but also reduces the productivity.

Chow and Watson's method offers the subsequent quantification of carbon fractions. CC is directly measured by the acidification and then OC and EC are quantified on the same filter punch with the thermal/optical protocol in the carbon analyzer.^{1,20} However, the fumigated acids and the dissociated anions (Cl^- ion from HCl) would not entirely evaporate and thus reside on the filter punch after the acidification. Fumigation with HCl can lead to intense charring phenomena in the ambient samples during thermal/optical analysis in an oxidizing atmosphere.¹⁷ Substitution of other non-halide containing acids such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) has other issues. The sulfate ion (SO_4^{2-}) and nitrate ion (NO_3^-) can decompose between 200 °C and 400 °C during the thermal/optical analysis and serve as oxidants for the prior oxidation of the pyrolyzed organic carbon (OP) and EC showing in our experiments. The subsequent quantification cannot work appropriately unless an alternative acid is found.

4. Conclusion

A good precision ($<3.8\%$) and accuracy (91.9%) have been demonstrated in the determination of carbonate for the aerosol

Table 3 Comparisons between the M-TOCA method and the method described in Chow and Watson¹

	The M-TOCA method	Chow and Watson's method
Instrumental design	An add-on device is connected to a thermal/optical carbon analyzer	A regular thermal/optical carbon analyzer
Acid	1 mL of 20% v/v H_3PO_4	20 μL of 0.4 M HCl
Sample size	A maximum of 20 pieces of filter punches (each of 0.5 cm^2)	Limitation of 1 piece of filter punch (0.5 cm^2)
Sample introduction	Sample punches are put in a vial and acidification takes place in the liquid phase; ultrasonic agitation	Sample punch is put on the quartz boat on the push rod in the carbon analyzer; acidification takes place on the filter punch; no ultrasonic agitation
Reaction environment	100% He at 40 °C with ultra-sonication	100% He without temperature control
Method MDL	0.028 $\mu\text{g cm}^{-2}$ or 0.057 $\mu\text{g C m}^{-3a}$	0.60 $\mu\text{g cm}^{-2}$ or 1.23 $\mu\text{g C m}^{-3b}$

^a The MDL in volume is calculated by assuming a sampling volume of 7.2 m^3 when a maximum of 20 filter punches (each of 0.5 cm^2) were used in each analysis. ^b The MDL in volume is calculated by assuming a sampling volume of 7.2 m^3 when a filter punch of 0.5 cm^2 was used in each analysis.

filter samples with the M-TOCA. The experimental results show that it is comparable with the results of the novel method using the regular TOCA. The method MDL for M-TOCA is significantly lowered because a larger sample size can be used in each run. It is thus more applicable to measure ambient samples having a low carbonate concentration. The M-TOCA also avoids the use of a strong acid, which can reduce the MnO₂ catalyst in the oxidizer and rapidly corrode the instrumental parts. In addition, the simple modification does not alter the instrumental structure for the regular thermal/optical analysis. Even though the M-TOCA cannot be applied to correct the individual thermal-defined carbon fractions from the CC contribution, it offers a sensitive, precise and accurate measurement for carbonate in filter samples.

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