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Ying S. Fung^a; Kwok L. Dao^a

^a Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

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DETERMINATION OF TOTAL CARBON IN AIR PARTICULATE MATTERS BY THERMAL COMBUSTION-ION CHROMATOGRAPHY

YING S. FUNG* and KWOK L. DAO

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

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A new analytical procedure based on Thermal Combustion-Ion chromatography was developed for an hourly determination of total carbon in air particulate matters using equipment readily available in the chemical laboratory. Optimised conditions were developed for both thermal combustion (oxygen flowrate at 100 ml min^{-1} for 15 minutes at 900°C), sampling of carbon dioxide generated (20 ml of 50 mM KOH with 10 drops of n-butanol as scrubbing solution) and carbonate determination by non-suppressed ion chromatography (0.6 mM potassium hydrogen phthalate as eluent), giving a working range of 0.1 to 40 mg-C l^{-1} or 20 to $800 \text{ } \mu\text{g-C}$ and a detection limit of 0.02 mg-C l^{-1} or $0.4 \text{ } \mu\text{g-C}$ using a 20 ml scrubbing solution and $0.2 \text{ } \mu\text{g m}^{-3}$ on hourly basis with a flowrate of 33 l min^{-1} . The method offers comparable analytical performance and wider working range as the conventional NDIR method which uses dedicated equipment. The reliability of the method has been established using graphite and various organic standard compounds with results showing satisfactory recoveries and good precision. Carbonaceous matters from the blank glass filters and the interference of other anions had been found not to affect the validity of the results. The method developed has been successfully applied for field studies at two selected sites in Hong Kong with commercial and industrial activities.

Keywords: Total carbon; air particulate matters; thermal combustion; indirect photometric detection; ion chromatography

INTRODUCTION

The recent rapid increase in traffic volume in many newly developed metropolis led to the concern about air pollution, in particular with regard to air particulate

*Corresponding author. Fax: +852-2548-2132. E-mail: YSFUNG@HKUCC.HKU.HK

matters due to their health effect and visibility reduction. Increasing amount of carbonaceous matters had been found in air particulate matters collected in urban areas^[1-2]. They were emitted from stationary and mobile sources as the result of incomplete combustion of fossil fuel. The major emitter was attributed to the increase in the number of diesel cars on the road due to preferential tax for the use of diesel fuel^[3]. As the result of incomplete oxidation of carbonaceous matters, many harmful chemicals were found in air particulate matters such as polyaromatic hydrocarbons as exemplified by the well known benzo(a)pyrene^[4-5]. Moreover, the respirable fraction of the total particulate matters was found to increase rapidly in urban particulate matters in recent years^[6], reflecting the increasing contribution of anthropogenic sources in urban areas. Thus, the monitoring of total carbon in air particulate matters becomes an important parameter to indicate the air quality in urban areas.

In order to provide a suitable parameter for carbonaceous matters, the total carbon should include both elemental carbons and semi-volatile organic compounds, as the amount of semi-volatile organic compounds indicates the potential health risk and the quantity of elemental carbons in air particulate matters strongly affects the visibility of the atmosphere^[7]. In addition to the capability of analysing both total carbons and semi-volatile organic compounds, the analytical method should have enough sensitivity to give time resolution at least on an hourly basis, with fast sample throughput in order to handle the large amount of analysis to be performed during a survey, and preferably using existing laboratory equipment so as to reduce the capital and running cost, as well as the cost associated for training laboratory staff for the use of new equipment dedicated for a given analytical task.

There are two major analytical approaches for monitoring carbonaceous matters in air particulate matters. The first approach is direct on-site monitoring and the second indirect determination via an oxidation route. For direct monitoring, the carbon content of the particulate matters sampled had been determined by photoacoustic photometry^[8-9], piezoelectric crystal^[10], and optical reflection method^[11]. Although direct detection is convenient to carry out and gives immediate results, dedicated equipment is needed. In addition, the method is not specific for carbonaceous matters (piezoelectric crystal and optical reflection) and only for elemental carbon (photoacoustic photometry).

For the indirect approach, thermal combustion is used to oxidise all carbonaceous matters collected on a filter under oxygen atmosphere to CO₂ prior to detection^[12]. This method is basically a laboratory procedure, which is simple to perform, provides information for both elemental carbons and semi-volatile organic compounds, and enables multi-point kerbside sampling of air particulate matters using simple air pumps and filters. With the use of a temperature

programmed furnace controlled at 350°C prior to stepping up to 900°C, the method can be used to determine both the organic and the elemental carbon fractions^[13] by collecting the CO₂ generated in different times from the stepwise oxidation of carbonaceous matters before IC determination.

The success of the thermal oxidation procedure depends on the mechanism to detect CO₂ generated upon oxidation of the carbonaceous matters. Methods had been developed using nondispersive infrared (NDIR) spectroscopy^[14], gravimetry^[11] and flame ionisation detection (FID) after reduction of CO₂ to CH₄^[15]. The NDIR and FID method give detection limits of about 1 µg carbon including the variation of the blank and use specific instruments not commonly available in most laboratories. The gravimetric method is only suitable for detecting high level CO₂ at mg quantity. Thus, a new, more sensitive and selective method using commonly available equipment is needed to be developed for the detection of the carbon dioxide generated during combustion.

The recent advance of non-suppressed ion chromatography using ordinary HPLC equipment provides a suitable method for the detection of carbon dioxide after it was scrubbed into solution and converted into carbonate anion^[16-17], as it provides a highly sensitive method to determine ppm level of carbonate with the selectivity needed to detect the carbonate peak against the interference of other anions. In the present work, the effectiveness of the thermal combustion method for oxidising carbonaceous matters was studied. The non-suppressed IC procedure was optimised for carbonate determination and for matching with the requirement of the thermal combustion method. The applicability of the thermal combustion-IC procedure developed was investigated in a field survey conducted at two selected sites in Hong Kong.

METHODS AND PROCEDURES

Reagents and Standard Solutions

All chemicals used were analytical reagent (AR) or equivalent grades and they were used as received. The oxygen gas (Hong Kong Oxygen Ltd.) was purified by passing through an activated carbon column and a soda asbestos column prior to use. The stock anion standard solutions (1000 mg l⁻¹) were prepared by dissolving the corresponding potassium salts in doubly quartz distilled water.

Equipment and Apparatus

The ion chromatograph consisted of a Gilson 305 high pressure isocratic pump, a Rainin electronic module, a SSI Lo-pulse damper, a Rheodyne Model 7125

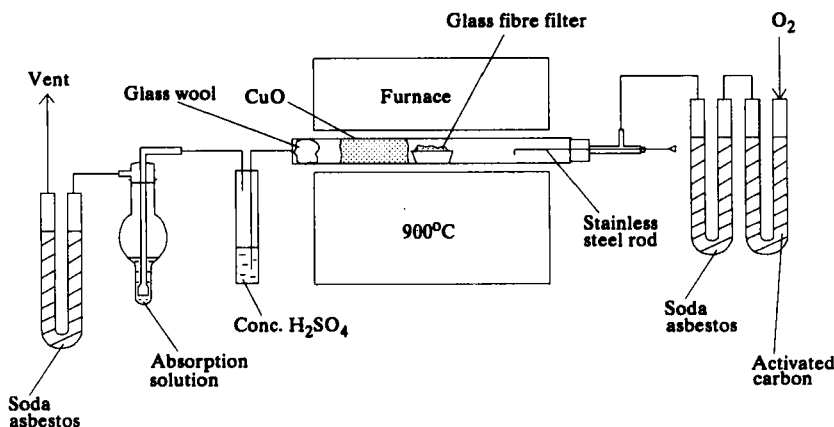


FIGURE 1 A schematic diagram of the thermal combustion apparatus

injection valve fitted with a 100 μ l sample loading loop, a stainless steel guard column (25 mm l. \times 4.6 mm i.d.) packed with PRP-1 resins, a Hamilton PRP-X100 anion-exchange column (15 cm l. \times 4.6 mm i.d.), a Milton Roy SpectroMonitor 3100 variable wavelength detector and a Hewlett-Packard 3393A integrator.

The apparatus for thermal combustion of air particulate samples was shown in Figure 1. It was mostly made up of glass except the combustion boat and combustion tube (66 cm l. \times 33 mm i.d.), both of which were made up of alumina capable of with-standing temperature up to 1500°C. All glass-wares were connected with tygon tubing. A plug of glass wool was placed at the exit end of the combustion tube in front of a length of 10 cm granular cupric oxide. A H₂SO₄ bath was added before and a soda asbestos column after the absorption solution so as to remove potential interferents entering the scrubbing solution.

Sampling and Analytical Procedures

The sampling points were set at the selected sampling location at the height of the breathing zone near the edge of the pavement facing the road. A diaphragm pump with gas flowrate set at 33 l min⁻¹ was used to sample air particulate matters onto a plastic holder containing a 47 mm diameter preconditioned glass filter. The filters were replaced hourly and samples were taken from 8:00 a.m. to 6:00 p.m. The filters were immediately sealed inside the plastic holders after each sampling. The sampling rate for each filter is estimated as the mean of the recorded air flow at the start and the end of the sampling period in order to compensate for the variation of flowrate during sampling. The sampling time was

chosen to be one hour so as to reduce the timing error caused by manual changing of the filters. During the sampling period, the number of automobiles passing through the sampling point was counted hourly for every 5 min at the beginning of each sampling hour and no attempt had been taken to distinguish the different types of automobiles. The particulate-loaded filters were conditioned in the desiccator for one hour, weighed and stored in a refrigerator at 4°C prior to analysis.

For thermal combustion, the particulate-loaded filter was folded, placed onto a preheated combustion boat and inserted into a preconditioned combustion tube. Purified O₂ at a flowrate of 100 ml min⁻¹ was then passed for 3 min to remove any residual CO₂ trapped inside the combustion tube. At the end of the O₂ purging, the scrubbing solution (20 ml of 50 mM KOH) was added to the scrubber together with 10 drops of n-butanol to enhance CO₂ absorption. The boat was then slowly pushed to the centre of the heating zone by a stainless steel rod and kept for 5 min. After the combustion was complete, the scrubbing solution was transferred to a volumetric flask, which was then made up to 25 ml with the eluent prior to IC analyses.

For IC analysis, the eluent and samples were filtered through a 0.45 μm membrane filter before use. The eluent (0.6 mM potassium hydrogen phthalate) was made up to concentration using doubly quartz distilled water with pH adjusted to 9.5 using 0.1 M KOH solution. The flowrate of the eluent was maintained at 1 ml min⁻¹. The wavelength for detection was selected at 272 nm and the reference loop of the detector was filled with the eluent to enhance the sensitivity.

Quality Assurance and Safety

The quality assurance procedures include the following: preconditioning of glass filters before and after sampling, precleaning of combustion boat and combustion chamber, setting up of standard sampling and storage procedure, determination of field blank and reagent blank, and calibration of the combustion and IC equipment using standards during each analysis.

For preconditioning of filters, the 47 mm glass fibre filters were preheated at 500°C for two hours and cooled to room temperature in a desiccator prior to weighing and sampling. After sampling, the filters were preconditioned in a desiccator for one hour prior to weighing and storage. The combustion tube and combustion chamber were preheated at 900°C for an hour and cooled under oxygen gas purging prior to use. The system must be purged with oxygen for at least 3 minutes prior to the introduction of the absorption solution and samples.

The standard sampling and storage procedures include measuring gas flowrate onsite before and after each sampling, mandatory procedure of using plastic glove to handle filters both in the field and in the laboratory, consistent folding procedure for glass filters with inward folding of particulate-loaded side, standard preconditioning of filters prior to weighing and storage in a refrigerator at 4°C.

The field blanks were obtained by taking two unexposed filters from the same batch of glass filters during each sampling at a given site and stored under identical conditions as the samples prior to combustion-IC analysis. Reagent blanks for IC determination were made up of unexposed absorbing solution following the same procedures as the samples. The combustion efficiency was monitored using graphite standards. Calibration curve using carbonate standards was prepared prior to each sample chromatographic run. All carbonate standards were prepared using eluent as the diluent in order to reduce the matrix interference and to minimise the presence of the blank carbonate peak.

Good Laboratory Practice should be followed, in particular for safety measures during thermal combustion. The gas flowrate should be monitored and adjusted during the experiment to avoid a sudden surge of the pressure in the system, which could lead to the spillage of concentrated sulphuric acids and the alkali absorption solution. Particular attention should be paid while the apparatus was heating up or cooling down to ensure that a constant flowrate of oxygen was maintained during the heating and cooling cycle.

RESULTS AND DISCUSSION

Investigation of Thermal Combustion Process

Glass fibre filters^[18] were chosen to collect air particulate matters due to their low organic carbon content and reasonable cost. As organic matters present in the glass filter could contribute to the blank total carbon content, it could affect the detection limit of the analytical method developed. Thus, the blank total carbon content (TC) of the filters were determined and methods to reduce it investigated. Preconditioning the glass filter by heating it at 500°C for 2 hours was found to be an effective way to reduce the residual TC content. As the TC content may vary with different batches of glass filters, the TC content of three glass filters randomly selected from eight batches of glass filters was determined with results given in Table I showing that the mean TC of each filter from different batches was $1.09 \mu\text{g cm}^{-2}$ with mean standard deviation of $0.04 \mu\text{g cm}^{-2}$. The TC content of the glass filter was found to be low and fairly constant with less than 5% variation amongst different batches of glass filters.

TABLE I Total carbon content in glass filters

Batch no.	TC found ^a ($\mu\text{g cm}^{-2}$)	Std. Dev. ($\mu\text{g cm}^{-2}$)
1	1.06	0.04
2	1.12	0.05
3	1.11	0.04
4	1.08	0.03
5	1.13	0.05
6	1.13	0.05
7	1.05	0.04
8	1.07	0.04
Mean	1.09	0.04

^a Mean of triplicate analyses.

To optimise the conditions of combustion, the effect of oxygen flowrate and combustion time was investigated. Graphite powder weighed to 1 mg was dispersed in a pre-conditioned glass filter for use as a standard for recovery test under different conditions of combustion. The combustion temperature was kept constant at 900°C to ensure complete oxidation of all carbonaceous matters using the cupric oxide catalyst. The effect of the oxygen flowrate is shown in Figure 2. For high flowrate, the stripping efficiency of CO₂ is affected and for low flowrate, incomplete oxidation may occur within the combustion time of 15 min. Thus, an optimised flowrate was obtained at 100 ml min⁻¹ with recovery close to 100% using 1 mg graphite standard. Table II shows the results for the recovery of graphite at different combustion times. To ensure complete recovery of 1 mg graphite loaded on a clean filter, the combustion time should be kept not less than 15 minutes. To maximise the sample throughput and ensure complete combustion, the oxygen flowrate was kept constant at 100 ml min⁻¹ and the combustion time at 15 min for subsequent studies.

To test the combustion efficiency for different types of carbonaceous compounds, four organic standards were chosen for the investigation, including both elemental carbon (graphite), organic polyaromatic hydrocarbon (anthracene) and high boiling oxygenated carboxylic acids (benzoic acid and hexadecanoic acid). The inorganic carbonate compounds were not included in the present study as too high a temperature is needed for their thermal decomposition. Recovery data for the organic carbonaceous compounds are given in Table III. All the organic compounds investigated were giving satisfactory recoveries and good precision with average recoveries greater than 96% and relative standard deviation less than 5%. The method is thus suitable for the analysis of total carbons in organic compounds.

Development of Ion Chromatographic Procedure

The potassium hydrogen phthalate system was chosen as the eluent for the present work due to its strong absorption at 272 nm^[19] and good separation of simple anions^[19, 21]. The pH of the eluent was normally adjusted to between 5 and 6 for the separation of common anions^[21]. However, inorganic carbons exist mainly as $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ in acidic solution, which are weakly dissociated and show nearly no retention on the analytical column. Thus, the separation must be done under alkali condition with CO_3^{2-} as the primary ion as its highly effective nuclear charge could significantly increase its retention on the column. Results of our previous work^[16, 17] indicated that the best separation for carbonate occurred

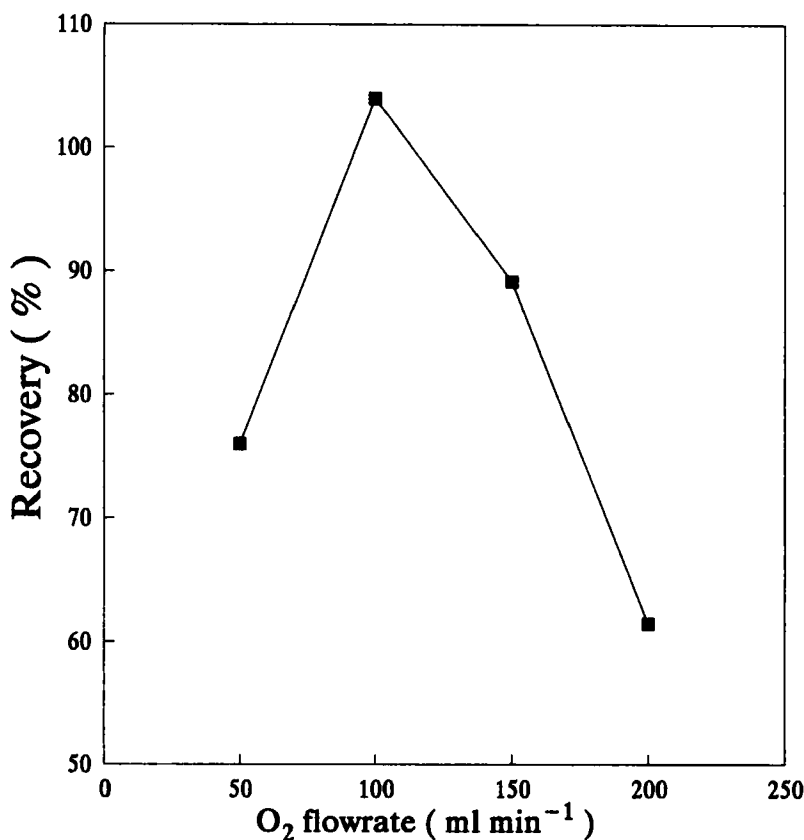


FIGURE 2 The effect of the oxygen flow rate on the recovery of graphite

TABLE II Recovery of graphite standard from thermal combustion at different combustion times

Combustion time ^a at 900°C (min)	Recovery ^b (%)
5	66.5
10	85.0
15	104
20	99.3
25	96.5
30	97.5

^a Oxygen flowrate = 100 ml min⁻¹. ^b Mean of triplicate analyses.

TABLE III The recovery of different carbonaceous compounds

Standard	Weight added (mg)	Recovery (%)	Recovery: Mean (%) (RSD, %)
Graphite	1.05	97.1	97.8
	0.54	94.4	(3.9)
	1.11	102	
Hexadecanoic acid	1.19	93.3	95.7
	1.51	99.1	(3.0)
	2.23	94.6	
Benzoic acid	0.90	93.5	98.3
	1.60	97.3	(5.3)
	1.77	104	
Anthracene	0.97	97.8	96.4
	1.41	96.2	(1.3)
	1.12	95.3	

under eluent with 0.6 mM KHP at pH 9.5. Thus, this eluent was used for the present work.

As the retention times of the NO₃⁻ and SO₄²⁻ peaks are close to the CO₃²⁻ peak^[16, 17], potential interference is indicated. The effect of NO₃⁻ and SO₄²⁻ on CO₃²⁻ determination is thus studied. Relative error of over 10% was observed in the determination of 50 mg l⁻¹ CO₃²⁻ in the presence of 500 mg l⁻¹ NO₃⁻ or SO₄²⁻. However, the amounts of NO₃⁻ and SO₄²⁻ present in the absorption solution after thermal combustion of particulate-loaded filters were found during the field work to be less than 50 mg l⁻¹ so that the error in the determination of CO₃²⁻ concentration caused by these interferents would not be exceeding 3%.

Using the IC procedure developed^[17], the calibration curve of standard CO₃²⁻ using peak area integration showed good linearity with correlation coefficient of 0.9994 in the linear range varying from 0.5 to 200 mg l⁻¹ and 0.1 to 40 mg l⁻¹ for the determination of carbonate and TC respectively. This corresponds to a

total weight of 2 to 800 μg carbon if 20 ml scrubbing solution was used. Based on the noise of the IC chromatogram, the detection limit (signal/noise = 2) was 0.1 or 0.02 mg l^{-1} for carbonate and TC respectively, and for total weight, 0.4 μg carbon for 20 ml scrubbing solution. Considering the contribution of background TC from both IC (0.4 μg) and filter blank (1 μg) using 20 m^3 air sample collected hourly, the detection limit of the overall procedure is 0.1 $\mu\text{g m}^{-3}$. All the CO_3^{2-} standards were prepared using eluent as the diluent in order to reduce the matrix interference and to minimise the presence of the blank CO_3^{2-} peak. The relative error and relative standard deviation obtained in five determinations of 50 mg l^{-1} CO_3^{2-} standard solution were found to be 0.6% and 1.9% respectively.

The working range of the Combustion-IC procedure is dependent on the volume and capacity of the absorption solution for CO_2 . When 20 ml absorption solution was added to the scrubber and graphite powder was used as the sample, recoveries above 98.7% were obtained for samples below 2.4 mg and above 97.8% for samples up to 6.4 mg. Over 90 % recovery was obtained for filters containing graphite up to 10 mg carbon before the breakthrough of the absorption solution occurred. However, considering the upper linear range of the IC method, the corresponding working range for total carbon determination using 20 ml scrubbing solution was found to vary from 2.5 μg to 1 mg and the detection limit was 0.5 μg . Thus, the upper limit is controlled by the IC working range. Although the upper working range can be extended by increasing the volume of absorption solution, this is not necessary for any of the samples we have analysed because the total carbons found in all the collected samples was ranging from 40 μg to 1 mg. For the lower limit, it is mainly controlled by the residual carbons in the blank, as the sensitivity of the IC method is more than adequate for the task required. For the use of the 47 mm diameter glass filters, about 17 μg of carbon with 4% relative standard deviation (or about 1 μg carbon for one standard deviation) were obtained as indicated by the results given in Table 1. The blank value was subtracted from the analytical results and the uncertainty involved is acceptable in face of the lower working range of 40 μg total carbons collected by the filters.

Applicability study of the Thermal Combustion-IC Procedure

An applicability study of the thermal combustion-IC procedure for TC determination in air particulate matters was carried out in two selected sites in Hong Kong (Figure 3). Due to the presence of a large number of vehicles on a limited length of road, the high population density, the very narrow street restricting effective dispersion of air particulate matters, and the intermixing of

residential, commercial and industrial areas, there are frequent complaint about particulate pollution emitted from diesel cars in Hong Kong. Thus, the first site was selected at Tsimshatsui (TST), a mixed commercial and residential area. The sampling point was set near the edge of the pavement facing a busy road. The area is fairly close to the sea and near the entrance of the cross-harbour tunnel. The second site was selected at Kwun Tong (KT), a heavily industrialised area fairly close to the sea and the airport. The sampling point is facing an extremely busy street with many heavy diesel vehicles passing next to the sampling point

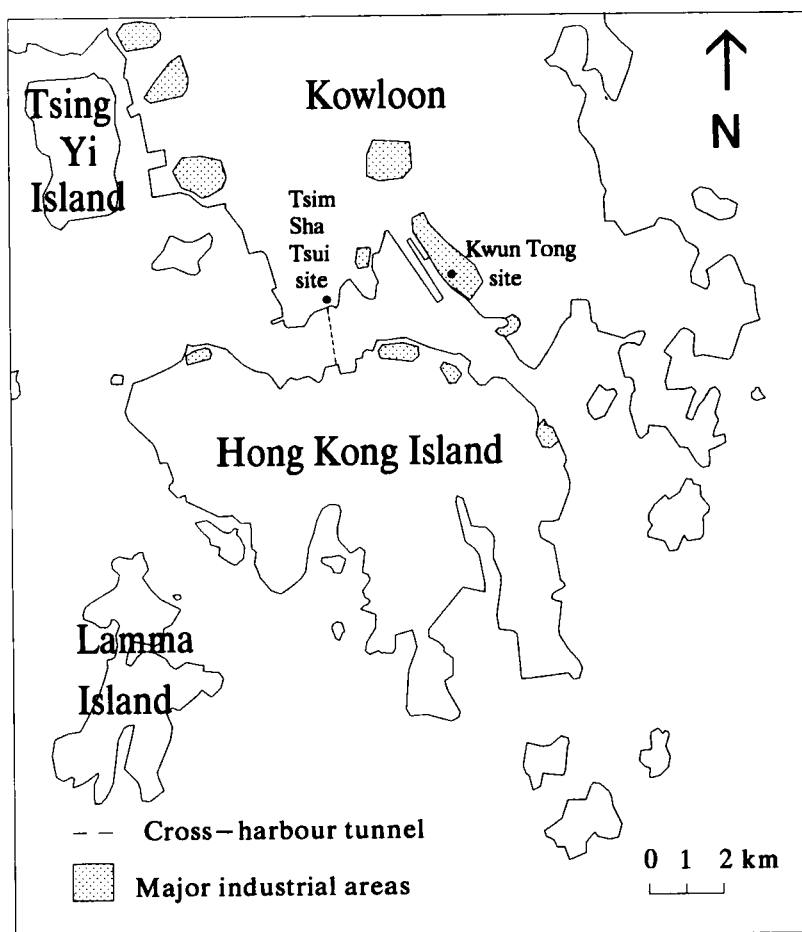


FIGURE 3 Map showing the two selected sampling sites

during office hours. Each site was sampled for four days during summer months, including week-days and public holidays.

The results on the hourly variation of TC at the two sites are shown in Table IV. In general, the average TC content found in the two sampling sites were high with means of 197 $\mu\text{g-C}$ and 263 $\mu\text{g-C}$ for the TST and KT site respectively. The particulate matters collected at the KT industrial site is shown to contain higher TC (263 vs 197 μg), more constant source (RSD: 27% vs 50%), and lower TC per car ratio (0.14 $\mu\text{g-C/car}$ vs 0.25 $\mu\text{g-C/car}$) as compared to the residential/commercial site (TST). This may be due to the larger volume and much faster traffic, and hence better dispersion at the industrial site.

Comparing the number of cars passing per hour at holidays (Sunday) and weekdays (Thursday, Friday and Saturday) at the KT site (Table IV), the average number was nearly three times higher in weekdays as compared to holiday. However, there are no obvious difference for weekdays (Tuesday and Wednesday) and holidays (Sunday and Monday) at the TST site. This reflects the difference in the pattern of vehicle activities at these two sites. A clear rush-hour peaks (8 to 10 am and 3 to 6 pm) were identified during weekdays at the KT site, but no clear pattern during holiday. For the TST site, the rush-hour pattern is not clear during both weekdays and holidays. For the correlation of the number of cars to the TC contents (Table IV), a good correlation was shown during holidays at the TST site, presumably due to the very slow traffic at the sampling site. However, poor correlation was obtained during both holiday and weekdays at the KT site. This confirms that additional sources of carbon were present at the KT site.

CONCLUSIONS

A new analytical procedure based on Thermal Combustion-Ion Chromatography was developed to enable hourly determination of total carbon in air particulate matters for field investigation using equipment readily available in the chemical laboratory. Optimised conditions were developed for both thermal combustion, sampling of carbon dioxide generated and carbonate determination by non-suppressed ion chromatography. The best combustion conditions were passing oxygen at a flowrate of 100 ml min^{-1} for 15 minutes at 900°C to achieve complete oxidation of both carbonaceous matters and semi-volatile organic compounds. Satisfactory sampling of the carbon dioxide generated was obtained using 20 ml of 50 mM KOH as the scrubbing solution with the addition of 10 drops of n-butanol. The IC procedure for the determination of carbonate was optimised to reduce the interference of nitrate and sulphate and to enable

DETERMINATION OF TOTAL CARBON

TABLE IV The daily average of total carbons in air particulate matters collected in two sampling sites under various environmental conditions

A. For Tsimshatsu site		Weather condition		Temperature range (°C)		TC ($\mu\text{g m}^{-3} \text{h}^{-1}$)		Average no. of car passing per hour		R ^b
Sampling day	Weather condition	Temperature range (°C)	mean	RSD (%)	mean	RSD (%)	Average no. of car passing per hour	R ^b		
Sunday	rainy	16-17	163	49	786	0.665				
Monday ^a	fine	18	179	25	618	0.885				
Tuesday	fine	19-20	249	51	804	-0.246				
Wednesday	fine	20	197	73	968	-0.052				
Average mean			197	50	794					
B. For Kwun Tong site										
Sampling day	Weather condition	Temperature range (°C)	TC ($\mu\text{g m}^{-3} \text{h}^{-1}$)		Average no. of car passing per hour		R ^b			
Thursday	fine	27-28	mean	RSD (%)	2282	0.161				
Friday	fine	27-30	212	48	2250	0.108				
Saturday	fine	27-30	241	16	2133	0.215				
Sunday	fine	25	399	30	882	0.061				
Average mean			201	15	1884					
			263	27						

^a Public holiday. ^b Correlation coefficient of traffic volume against total carbon content

determination of TC with a working range of 0.1 to 40 mg-C l⁻¹ or 20 to 800 µg-C and a detection limit of 0.02 mg-C l⁻¹ or 0.4 µ-C using a 20 ml scrubbing solution. The detection limit of the overall procedure was 0.1 µg m⁻³ using 20 m³ air sample collected hourly. The method offers a comparable analytical performance and wider working range as the conventional NDIR method which uses expensive and dedicated equipment.

The reliability of the method developed was established using graphite and various organic compounds as standards and all of them were giving results showing satisfactory recoveries and good precision. The contribution of carbons from the blank glass filters and the potential interference of other anions had been assessed and found not to affect the validity of the results. The method developed was applied for field studies at two selected sites in Hong Kong with commercial and industrial activities to obtain the TC content of air particulate matters collected on an hourly basis. The information obtained was found to be useful to indicate the sources of the carbonaceous matters, establish the daily pattern of TC due to vehicle and other related activities around the sampling site, and identify hot-spots with exceptionally high emission factor of carbonaceous matters on an hourly basis.

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