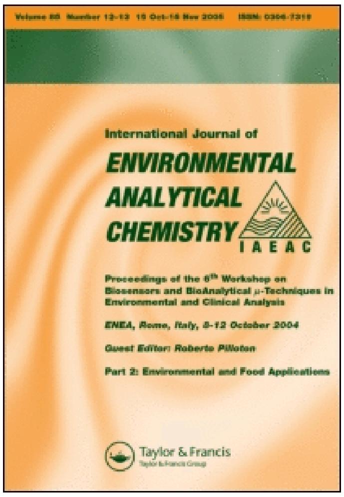

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AN ACCURATE, SIMPLE AND NOVEL ANALYTICAL METHOD FOR THE DETERMINATION OF TOTAL ORGANIC CARBON IN SEDIMENT

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An improvement to the Walkley-Black wet digestion method for accurate determination of total organic carbon (TOC) in mangrove and marine sediments was developed. Sediment samples were digested with acid dichromate in a domestic microwave for 7 minutes. The TOC results obtained from the proposed method were in excellent agreement with the conventional Walkley-Black method. The sediments were spiked with three standard organic compounds, at a fortification level (viz. 10 to 20 mg TOC). The mean recoveries of TOC for the proposed method ranged from 100 ± 4% (n=15) for standard reference materials of marine/coastal sediments to 101 ± 6% (n=30) for mangrove sediments. The relative standard deviation values of the proposed method were small, around 3 to 4%. These data demonstrate that the proposed method had a better performance than the conventional Walkley-Black method in terms of its simplicity, reproducibility, accuracy, precision and recovery.

Keywords: Total organic carbon; microwave digestion; dichromate oxidation; sediment

INTRODUCTION

The organic matter in the sediment can be quantified by the total organic carbon (TOC). The concentration of TOC found in sediments not only indicates the degree of organic pollution in water and sediment. It also plays an important role in the accumulation and release of different micro-pollutants. In order to compare the degree of pollution of different sediments at different locations with different composition, metal concentrations are often normalised to a conservative

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component[1–9]. TOC is an important normaliser that clearly distinguishes contaminated and uncontaminated sediment[1,2,8,9].

A wide variety of analytical procedures have been used for the determination of TOC in soils. The common types of analyses include titrimetric, gravimetric, and photometric methods in which either the amount of carbon dioxide produced or the amount of oxidants used in the process is measured. In some cases, if the oxidation of the organic material is not completed in the presence of an oxidant, the method would incorporate an average correction or conversion factor to determine the total organic carbon content[10]. The value of the correction factor needs to be determined experimentally for each type of samples concerned. One way to eliminate the correction factor is to improve the completeness of the oxidation process. Many more efficient analytical methods such as dry and wet combustion have been reported but they are costly and relatively time consuming. Modern dichromate methods involve a period of heating under reflux also improve the oxidation efficiency but this method is subjected to interference by oxidizable or reducible soil constituent such as Cl^-, Fe^{2+} and MnO_2. Zlotorzynski[11] presented a review for the latest advance in the application of microwave radiation to the analytical and environment chemistry including digestion, extraction, chemical reaction, pre-concentration, and desorption of samples. With respect to soil and sediment studies, the adoption of microwave oven for sample digestion prior to analysis of metal contents is well documented[12,13]. A novel method for extraction of various types of labile compounds from food samples using a domestic microwave was developed by Ganzler and his co-workers[14,15] in 1986 and 1990. Jardim et al.[16] and Valle et al.[17] had also proposed microwave heating to determine COD (Chemical oxygen demand) concentrations in water and wastewater samples. Therefore, it is possible to achieve a complete oxidation of organic matter using microwave digestion in determination of TOC content in sediments.

Numerous rapid and accurate methods are available to determine the TOC content in sediment. However, it is important for the analysts to recognise the limitation and drawback of each method. Micro-combustion method has recently been introduced and numerous commercial analysers are available, but it is a costly method and requires skilful techniques to handle and maintain the instrument. Moreover, when analysing TOC in sediment[6,10] by the commercial analyser such as Leco-600–800–300 CHN-900 analyser and microbalance, the nominal sample size is 2 mg, much smaller than that used in the rapid dichromate titrimetric method (1–2 g of sample). The small sample size used would affect the accuracy and reliability of this technique especially if the particle size of the sediment is large or if the sample is quite heterogeneous. Another criticism of the CHN analyser is the shift of the signal after prolonged analysis so periodical replacement of the catalyst in the furnace is needed.

Despite the fact that analytical techniques for determining total organic carbon in soils are reasonably well established[18], analytical procedures concerning the more complex matrix in sediments such as mangroves are rarely addressed. Mangrove sediments, being intertidal, are periodically flooded with seawater by incoming tides but are exposed during the low ebb tide period. The sediments are reduced and anaerobic, with varied amounts of chlorides, irons, sulphide and organic matter[19]. These distinct features of mangrove sediments would affect the determination of TOC using traditional analytical procedures developed for terrestrial soils or other matrices.

Moreover, most studies concerning TOC measurements were standardized with the dry combustion which are normally considered to yield absolute value of total organic carbon in soils. Unlike the TOC and COD determination in water and wastewater samples which emphasize the percentages of recovery in spike samples[20,21], little information was reported on the recoveries of standard organic compounds spike in sediment samples although the matrix in sediments is often more complex than water samples. The goal of the present study is to develop a Microwave heating procedure, in comparison with the conventional (Walkley-Black) method[18] for determining the TOC concentrations in mangrove sediments. This method is a modified version of the COD determination developed by Valle and his co-workers[17]. The percentage of recovery by the proposed method after spiking the sample and standard sediments with different organic compounds will also be determined.

EXPERIMENTAL

Sampling

Surface sediment samples (0–3 cm) were collected from ten different mangrove sites in Hong Kong (Figure 1). In each mangrove site, duplicate samples were collected at every 5 or 10 m intervals along one transect from landwards to seaward regions and a total of four to five samples were collected per transect. Sediment samples were air-dried at room temperature (20 ± 2°C), disaggregated with a pestle and mortar, and sieved through a 2-mm mesh sized sieve to remove coarse particle. The sieved sediment samples were analysed for the percentages of TOC using the conventional Walkley-Black[18] and the proposed Microwave methods.

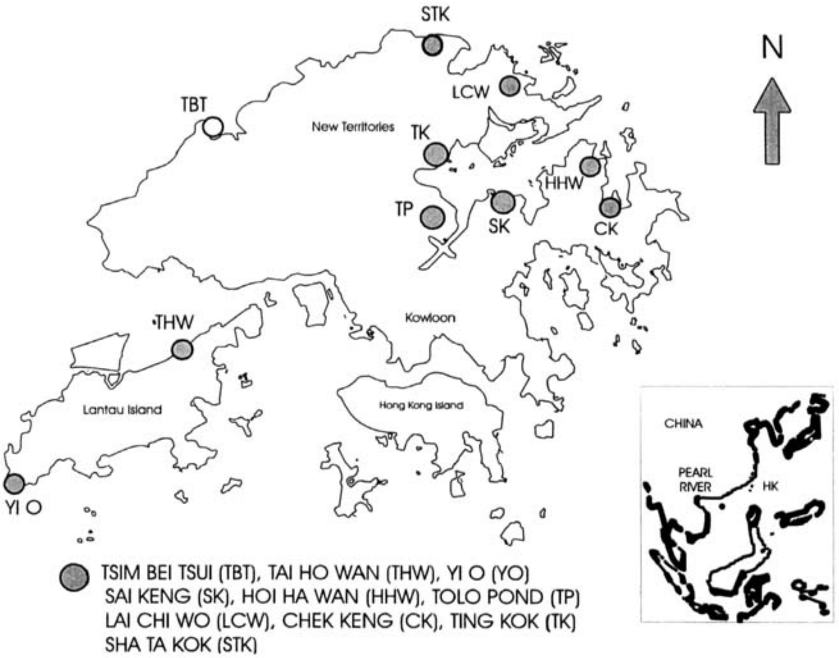

FIGURE 1 Map of Hong Kong showing the location of ten mangrove sampling sites

Apparatus

A turntable commercial domestic microwave oven (Sharp R4A52G) with an output power of 850W was used. The sample was digested in a 250 ml conical flask. A small glass funnel and marble were placed at the mouth of the conical flask to create a partial reflux condition.

Reagents

All reagents used were of analytical reagent grade quality, and all water was distilled and deionized using a Millipore water purification system.

1 N potassium dichromate was prepared by dissolving 49.04g $K_2Cr_2O_7$ in distilled deionised water and dilute to 1 litre.

Sulfuric acid-silver sulfate solution was prepared by dissolving 15 g of Ag_2SO_4 per litre of conc. H_2SO_4 and letting it stood overnight.

Titrant was prepared by dissolving 140g $FeSO_4.7H_2O$ in 500 ml water containing 15 ml concentrated H_2SO_4 then the cooled solution was diluted to 1 litre.

Ferroin indicator was prepared by dissolving 1.49g of 1,10-phenanthroline monohydrate and 0.7 g $FeSO_4.7H_2O$ in 100 ml water.

Phosphoric acid : 85% conc. H_3PO_4.

Analytical Methods

All glasswares were cleaned with soap and water and prewashed with boiling acid dichromate solution to prevent contamination.

The conventional TOC determination was carried out using 0.5-1g sample, according to the method of Walkley and Black[18].

The proposed microwave digestion was carried out by placing 0.5–1 g sample, containing 10 to 25 mg of organic C, into a 250 ml conical flask. 10 ml $K_2Cr_2O_7$ was added and the flask was swirled gently to disperse the sediments in the solution. Then 20ml conc. H_2SO_4-Ag_2SO_4 solution was added rapidly. A funnel and a marble were placed at the mouth of the conical flask. The mixture was ultrasonicated for a further 2 minutes. The flask was then placed into a plastic bucket, in which, small holes were cut at the wall of the bucket. In order to reduce damage to the magnetron of the microwave oven, 200 ml tap water (room temperature) was placed in the bucket to absorb any acid fume produced during microwave heating. In addition, a 100 ml beaker containing 80 ml tap water was also placed in the oven to further reduce acid attack and used to indicate the boiling condition. Three samples were digested in a domestic microwave at the maximum power for 7 minutes. All the digestion procedures were carried out in a fume hood. After the digestion, distilled deionised water was immediately added to the hot digested mixture in order to quench the reaction, the resulting solution was about 200 ml by volume. After cooling, 10 ml $H_3PO_4$was added, the remaining dichromate was determined by stirring the sample on a magnetic stirrer. The stirred sample was titrated with Iron (II) solution using 3 to 4 drops ferroin indicator.

Two blank determinations were carried out to allow for any thermal decomposition of the dichromate which was taken into account for the calculation of the TOC value. For the next cycle of microwave heating, fresh tap water at room temperature would replace the hot boiling water in order to keep a constant operating condition in a batch-wise analysis.

Recoveries Study with Marine Sediment

TOC-fortified environmental samples were selected from each sampling point. They were spiked with standard organic compounds (in powder form) to give a final concentration at which about 75 % dichromate will be reduced before back titration with titrant. Three analytical reagent grade organic compounds, namely, potassium hydrogen phthalate (KHP, $HOOCC_6H_4COOK$), propyl p-hydroxybenzoate (p-BA, $HO\text{-}C_6H_4COOCH_2\ CH_2\ CH_3$) and 1-naphthol (1-Nap, $C_{10}H_8O$, with 2 aromatic rings) were spiked directly into the selected mangrove sediment samples and the standard reference materials (SRMs) of the marine and coastal sediments. As the sediment may contain high matrix interference such as oxidizable or reducible compounds, three organic standard compounds were also spiked into fine sand (BDH grade with 40 to 100 meshes, very low in Fe content) to further verify the methods.

TABLE I % TOC present in mangrove and marine sediments determined by conventional Walkley-Black Method

Sampling site / SRM	*No. of determinations*[a]	*TOC, %*			
		mean	*range*	*std dev.*	*Rel std dev, %*
LCW	10	1.03	0.4–1.9	0.5	52
STK	3	1.06	0.9–1.4	0.3	28
TBT	8	1.10	0.9–1.3	0.1	12
CK	8	1.15	0.8–1.7	0.3	26
HHW	6	1.15	0.9–1.6	0.3	25
TK	10	1.23	0.5–2.8	0.8	64
TP	10	1.65	0.7–2.5	0.6	35
SK	10	1.69	0.2–3.4	1.1	67
THW	11	3.71	2.1–4.6	0.9	25
YO	10	4.93	0.1–22	8.5	173
SRM (1646), USA.	3[b]	2.03	2.02–2.07	0.03	1.4
SRM (BCSS-1), CANADA	3[b]	2.06	1.99–2.11	0.06	3.0
SRM (MESS-2), CANADA	3[b]	1.37	1.33–1.41	0.04	2.7
SRM (PACS-1), CANADA	3[b]	4.08	4.00–4.22	0.12	2.9
SRM (GBW07313),PRC.	3[b]	0.32	0.30–0.38	0.05	14

[a] All samples of surface sediment were collected along one transect.
[b] Number of replicates.

RESULTS AND DISCUSSION

A preliminary screening of %TOC in mangrove sediments and the SRM sediments using the conventional Walkley-Black method was summarized in Table I.

Ten different mangrove sites were collected in Hong Kong, namely Lai Chi Wo (LCW), Sha Ta Kok (STK), Tsim Bei Tsui (TBT), Chek Keng (CK), Hoi Ha Wa (HHW), Ting Kok (TK), Tolo Pond (TP), Sai Keng (SK), Tai Hoi Wan (THW), and Yi O (YO). Five SRMs of marine and coastal sediments were used to study the precision of the Walkley-Black method. They were SRM1646 (Estuarine sediment from National Bureau of Standard, Washington DC), BCSS-1 (Coastal marine sediment from National Research Council, Canada), MESS-2 (Estuarine sediment National Research Council, Canada), PACS-1 (Harbour marine sediment from National Research Council, Canada) and SRM-GBW 07313 (Marine sediment from People's Republic of China). The RSD values for the SRMs except those from PRC were small (less than 3%) suggesting the Walkley-Black method was reproducible. However, there is no SRM of sediment available in the market include the certified TOC value. Therefore, it is difficult to know the accuracy of the proposed method. The aim of using SRMs in my study is to understand and pin-point whether this method is applicable to marine and coastal sediments. On the other hand, large RSD values were obtained from the mangrove sediments, probably due to the inherent heterogeneity of the sediments and the spatial variations of TOC concentrations in different mangrove sites in Hong Kong.

Optimization of Microwave Digestion Conditions

The microwave digestion period was studied by determining the % TOC in two mangrove sediments THW24b and YO13b at three different microwave digestion times: 3, 7 and 10 minutes. Our experimental results showed that 7 minutes was the optimum digestion period (Table II) as there was no significant difference between the TOC content in samples digested for 7 and 10 minutes. These two digestion times produced higher TOC values than that digested for 3 minutes. Besides, the optimum number of samples used per cycle was found by digesting reagent blank and sample THW24b individually at a condition of 1 sample/cycle, 2 samples/cycle and 3 samples/cycle for 7 minutes (Table II). It was found that 3 samples per cycle were the good operating condition because the % TOC obtained by 2 and 3 samples per cycle showed similar values. A comparable result was also found in the blank digested in 2 and 3 samples per cycle, while the temperature appeared to be too high and oxidized all dichromate in the blank when 1 sample per cycle was used.

Precision

The precision of the Walkley-Black and proposed microwave method for TOC determinations was evaluated by calculating the mean, standard deviation and relative standard deviation (%RSD). The precision of the two methods as expressed in terms of RSD was comparable according to the student t-test ($p=0.589$ for mangrove sediments collected from 10 sites, and $p=0.310$ for SRM samples). The F value of the analysis of variance test ($F=0.559$, $p=0.474$) also show that there was no significant difference between two digestion methods in terms of the RSD values of the mangrove samples. The RSD values were all below 10% (Table III) and the precision was satisfactory. However, RSD value was influenced by the concentration of TOC especially when the sample had a low TOC values, so the low detection limit of TOC by the titrimetry might also contribute to a large RSD value[22]. In addition, constant and low RSD values (< 5%) were appeared in all the SRMs samples except the one purchased from China (GBW07313) which also had the lowest TOC value among all SRMs.

TABLE II Optimization of digestion condition for Proposed Microwave Method

Sample	*Digestion condition*	*TOC % (Mean ± SD[a])*
Effect of digestion time (3 samples per cycle)		
THW24b	3 min.	3.44 ± 0.12
	7 min.	4.57 ± 0.15
	10 min.	4.45 ± 0.23
YO13b	7 min.	0.33 ± 0.06
	10 min.	0.36 ± 0.06
# of samples per cycle (7 minutes digestion time)		
THW24b	1	4.84[b]
	2	4.78 ± 0.11
	3	4.33 ± 0.15
Blank	1	ND.[c]
	2	19.93 ± 0.04
	3	20.05 ± 0.05

[a] Standard deviation, n = 3.

[b] n = 1.

[c] the titration condition could not be done as the dichromate had been oxidized completely at such high temperature.

TABLE III Comparison of Walkley-Black Method with the Proposed Microwave Method

Sampling site / SRM	*Walkley-Black[a], m(A) TOC, %*		*Proposed Method (B) TOC, %*		*Correction factor B/A*	
	Mean ± SD[b]	*RSD[c](%)*	*Mean ± SD*	*RSD(%)*		
YO13b	0.22 ± 0.012	5.5	0.33 ± 0.056	17.0		1.50
TK12a	0.53 ± 0.073	13.8	0.67 ± 0.091	13.6		1.26
STK110	0.63 ± 0.042	6.7	0.79 ± 0.092	11.7		1.25
TBT14a	0.79 ± 0.012	1.5	1.11 ± 0.038	3.4		1.41
HHW23b	0.79 ± 0.060	7.6	0.95 ± 0.020	2.1		1.20
CK23	0.84 ± 0.010	1.2	0.97 ± 0.057	5.9		1.16
LCW19b	1.55 ± 0.090	5.8	1.86 ± 0.032	1.7		1.20
TP12a	1.59 ± 0.068	4.3	1.88 ± 0.032	1.7		1.18
SK22a	1.63 ± 0.153	9.4	2.22 ± 0.232	10.5		1.36
THW24b	3.33 ± 0.110	3.3	4.57 ± 0.152	3.3		1.37
					Mean	1.29
					Std. dev.	0.11
					RSD (%)	8.8
SRM, PRC (GBW07313)	0.24 ± 0.034	14.2	0.37 ± 0.027	7.3		1.54
SRM(MESS-2)	1.03 ± 0.028	2.7	1.58 ± 0.046	2.9		1.53
SRM(1646)	1.53 ± 0.021	1.4	1.96 ± 0.023	1.2		1.28
SRM(BCSS-1)	1.55 ± 0.046	3.0	2.21 ± 0.020	0.9		1.43
SRM(PACS-1)	3.07 ± 0.090	2.9	4.03 ± 0.092	2.3		1.31
					Mean	1.42
					Std. dev.	0.12
					RSD (%)	8.5

[a] Calculation of the % TOC do not incorporate correction factor 1.33.

[b] Standard deviation, n = 3.

[c] Relative standard deviation.

TABLE IV Percentage of recovery in sample spiked with different standard organic compounds as determined by the conventional Walkley-Black Method (applied correction factor, 1.33)

Sampling site/SRM	*KHP*					*p-BA*					*1-NAP*				
	Sample TOC (A)	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*	*Sample TOC (A)*	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*	*Sample TOC (A)*	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*
YO13b	2.93[a,b]	10.92	13.85	16.38[a,b]	118	2.86	10.13	13.00	15.58	120	3.81	20.00	23.81	23.67	99
TK12a	4.38	15.44	19.82	21.27	107	4.54	16.07	20.61	13.48	65	4.44	16.42	20.86	23.47	113
STK110	2.41	15.39	17.80	21.67	122	2.88	16.33	19.21	22.67	118	6.49	16.75	23.24	24.77	107
TBT14a	5.35	14.40	19.75	23.17	117	4.85	13.13	17.98	18.77	104	5.47	12.92	18.39	21.37	116
HHW23b	5.67	14.21	19.88	22.37	113	6.01	17.60	23.61	22.37	95	5.00	19.50	24.50	22.67	93
CK23	4.44	15.15	19.59	22.37	114	5.26	14.13	19.40	22.07	114	4.48	23.92	28.40	26.86	95
LCW19b	4.09	14.49	18.59	21.07	113	4.48	13.53	18.01	14.98	83	6.21	15.08	21.29	18.07	85
TP12a	4.51	14.78	19.28	22.07	114	6.42	17.40	23.82	21.79	92	4.11	13.67	17.78	20.17	113
SK22a	4.73	13.98	18.71	23.17	124	5.03	14.53	19.56	20.47	105	4.53	14.75	19.28	21.47	111
THW24b	4.64	14.82	19.46	22.27	114	4.66	19.60	24.26	26.36	109	4.44	16.08	20.52	24.86	121
Mean ± SD.					116 ± 4.8					100 ± 17					105 ± 11.8
RSD (%)					4					17					11
GBW07313	2.24	10.54	12.78	14.08	110	2.15	10.87	13.02	15.48	119	2.48	9.00	11.48	11.88	103
MESS-2	3.13	15.72	18.85	22.07	117	2.97	16.13	19.10	19.47	102	3.53	20.33	23.86	25.76	108
SRM1646	4.62	15.39	20.01	24.17	121	4.93	18.73	23.66	28.66	121	3.85	15.17	19.02	21.47	113
BCSS-1	4.13	15.11	19.24	23.17	120	3.95	14.13	18.08	22.37	124	4.40	16.42	20.82	24.27	117
PACS-1	4.16	15.44	19.60	22.97	117	4.75	14.33	19.08	20.47	107	4.17	13.83	18.00	22.07	123
Mean ± SD.					117 ± 4.3					115 ± 9.5					113 ± 7.4
RSD (%)					4					8					7
Sand (control)	0	11.86	11.86	14.88	125	0	21.23	21.23	26.26	124	0	20.83	20.83	23.67	114

[a] Sample TOC and Experimental (mg) = weight of sample used (varied between 0.1 to 1 g) × 10 × %TOC. [b] All values except recovery were in mg TOC.

TABLE V Percentage of recovery in sample spiked with different organic compounds as determined by the Proposed Microwave Method

	KHP					*p-BA*					*1-NAP*				
Sampling site/SRM	*Sample TOC (A)*	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*	*Sample TOC (A)*	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*	*Sample TOC (A)*	*Spike value (B)*	*Theoretical (A)+(B)*	*Experimental*	*Recovery %*
YO13b	$3.24^{a,b}$	9.27	12.51	$11.79^{a,b}$	94	3.23	10.13	13.36	14.19	106	3.33	10.17	13.50	13.89	103
TK12a	3.90	16.28	20.18	17.49	87	3.55	17.33	20.88	21.10	101	4.42	17.33	21.75	21.10	97
STK110	3.14	14.92	18.06	17.42	96	2.43	17.33	19.76	21.40	108	4.91	18.92	23.83	25.23	106
TBT14a	5.67	15.29	20.96	19.97	95	5.33	15.80	21.13	22.37	106	5.54	15.50	21.04	21.77	103
HHW23b	5.19	14.07	19.26	18.40	96	5.05	15.80	20.85	22.22	107	4.38	14.25	18.63	20.35	109
CK23	3.69	16.24	19.93	19.07	96	3.87	15.00	18.87	19.90	105	4.06	16.83	20.89	22.45	107
LCW19b	5.51	13.74	19.25	19.82	103	5.01	15.67	20.68	19.90	96	4.09	13.25	17.34	18.55	107
TP12a	4.54	15.34	19.88	18.85	95	4.07	13.47	17.54	19.00	108	4.90	12.75	17.65	19.22	109
SK22a	4.50	14.92	19.42	18.85	97	3.82	15.73	19.55	20.65	106	5.49	15.25	20.74	21.55	104
THW24b	4.82	16.89	21.72	20.57	95	5.43	14.73	20.16	20.12	100	5.66	21.50	27.16	25.98	96
Mean ± SD.					95 ± 3.9					104 ± 4					104 ± 4.7
RSD (%)					4					4					4
GBW07313	2.81	10.16	12.97	12.76	98	2.80	13.27	16.07	16.59	103	2.44	10.08	12.52	12.91	103
MESS-2	4.37	15.01	19.38	18.32	95	4.02	16.37	20.39	20.72	102	4.03	15.25	19.28	20.05	104
SRM1646	4.18	15.01	19.19	19.85	103	5.22	17.20	22.42	21.70	97	3.91	13.50	17.41	18.70	107
BCSS-1	5.89	15.81	21.70	20.20	93	6.86	15.40	22.26	22.98	103	6.42	19.25	25.67	25.30	99
PACS-1	4.09	14.92	19.01	18.02	95	5.57	14.67	20.24	21.17	105	4.36	17.58	21.94	21.70	99
Mean ± SD					97 ± 4.2					102 ± 3.0					101 ± 3.7
RSD (%)					4					3					4
Sand (control)	0	11.72	11.72	10.89	93	0	21.73	21.73	22.90	105	0	20.50	20.50	19.82	97

[a] Sample TOC and Experimental (mg) = weight of sample used (varied between 0.1 to 1 g) × 10 × %TOC. [b] All values except recovery were in mg TOC.

Comparison of Walkley-Black and Proposed Method

The calculated correction factor for the 10 mangrove sediments (1.29) was not significantly different from that reported by previous workers (about 1.33)[18] (p=0.271). The slightly higher correction factor 1.42 obtained from the five SRMs was probably related to the fact that the SRMs purchased had a very small particle size (less than 63 μm). Most TOC measurement was done in samples just passed through a 0.2 mm sieve and it is not a common practice to determine TOC in sediment of such fine particle size as in the SRM. Both the student t-test and F values show that the TOC concentrations determined by the Walkley-Black method (using 1.33 as the correction factor) were not significantly different from those obtained by the proposed method (p=0.88 and 0.91 for sediments from 10 mangrove sites and SRM samples, respectively). These results confirm that the Walkley-Black and the proposed microwave methods were comparable, and the latter method was a more accurate and versatile technique. Charles and his co-worker[23] produced a complete review on the recovery studies of TOC measurements, comparing the wet oxidation values determined by the Walkley-Black method with those obtained by standard procedure of dry combustion. They found that the values obtained by these two methods were very close. In the present study, the relationship between the Walkley-Black and the proposed Microwave method was evaluated by linear regression analysis over the concentration range studied. The regression equation for TOC obtained by two methods were: $y = 0.7352x + 0.0379$, where x and y equal to Walkley-Black and proposed methods respectively. The coefficient of determination ($R^2 = 0.978$) were approached to one, implying that most of the data appeared in two methods were closely related to each other.

Accuracy and Recovery Studies

The accuracy of the two methods was evaluated by the recovery values approaching 100%. Tables IV and V summarize the recovery data obtained from spiked samples. The mean recoveries of KHP, p-BA and 1-Nap spiked into ten mangrove sediments determined by Walkley-Black method were 116, 100 and 105% respectively, and the corresponding recoveries for five SRMs samples were 117, 115 and 113% respectively. The abnormally high recovery data obtained by the Walkley-Black method could be attributed to the inclusion of a correction factor (1.33). The recoveries obtained by the proposed microwave method were more close to 100%, with recovery values of KHP, p-BA and 1-Nap spiked to the mangrove sediments equalled to 95, 104 and 104% respectively, and those for SRMs were 97, 102 and 101% respectively. Similar abnormally high recovery data (114–125 %) of the Walkley-Black method were also found in the sand sample (the control) whereas in the microwave method, relatively good recovery results ranging from 93 to 105% were obtained. Based on the recovery data obtained from spiking the samples with three organic compounds, the efficiency of dichromate oxidation by the Walkley-Black method was in the descending order: KHP (116% for mangrove sediments, 117% for SRMs and 125% for sand) > p-BA (100, 115 and 124% for mangrove, SRM and sand respectively) > 1-Nap (105, 113 and 114% for mangrove, SRM and sand respectively). The last compound (1-Nap) is considered as a refractory compound that possesses two aromatic rings, i.e. more difficult to oxidize. On the contrary, there was no significant difference in the recoveries of these three organic compounds when the proposed microwave method was used, suggesting that microwave digestion was a more complete oxidation procedure for determining TOC in mangrove and marine sediment. The relative standard deviations of the Walkley-Black method lay between 4 and 17% while a more constant RSD value (3 and 4%) was obtained by the proposed microwave method. These results demonstrate the completeness, effectiveness and preciseness of the proposed microwave digestion method in determining TOC content in sediments.

CONCLUSIONS

TOC concentration in sediment samples is an important parameter to most agronomists, ecologists, geologists and environmental chemists to assess the degree of pollution in an environment. As the Walkley-Black procedure often overestimates the % TOC in sediments, either due to incomplete oxidation of the carbonaceous material by chromous acid or due to the inclusion of an inaccurate correction factor, which varies according to the matrix of the sediments. If an experimentally determined correction factor was not available for a particular group of samples, the Walkley-Black method could only be considered as a semi-quantitative approximate method. The proposed microwave method was found to be an accurate, convenient, inexpensive, precise and rapid procedure to determine the TOC content in sediments. The proposed method could be applied to a wide range of mangrove sediments as well as SRMs of marine and coastal sediments. The recovery studies by spiking samples with different kinds of standard organic compounds demonstrate that the microwave digestion method was reliable with a mean recovery of 101 ± 5.4%, n=45. When comparing results between Walkley-Black and the proposed microwave digestion methods, the correction factor for the mangrove sediments was around 1.29, which was not significantly different from the value (1.33) commonly adopted for the determination of TOC in soil samples.

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