

Organic Carbon Determination in Acid Sulphate Soils

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Keywords: acid sulphate soils, carbon, Leco, total oxidation

ABSTRAK

Pirit adakalanya wujud di zon penurunan profil tanah asid sulfat. Pirit ini dipercayai mengganggu penentuan C_{org} di dalam tanah melalui kaedah pembakaran basah dengan menggunakan $Cr_2O_7^{2-}$. Satu kajian telah dilakukan untuk mencari satu kaedah tepat serta boleh dipercayai untuk taksir C_{org} dalam tanah asid sulfat di Malaysia yang mengandungi jumlah pirit yang berbeza. Beberapa kaedah penentuan karbon (C) yang mantap telah dibanding dengan kaedah standard, iaitu Carbon Determinator (Leco IR-312). Gangguan pirit di dalam penentuan C di dalam tanah asid didapati sedikit. Kaedah pengoksidaan total didapati sebagai kaedah yang paling tepat dan dipercayai untuk penentuan C_{org} di dalam tanah asid sulfat tanpa kehadiran Carbon Determinator. Kaedah Walkley-Black dan kehilangan melalui pembakaran masing-masing didapati kurang taksir dan terlebih taksir kandungan C_{org} dalam tanah.

ABSTRACT

Pyrite is almost exclusively present in the reduced zone of acid sulphate soil profiles. This pyrite is believed to interfere with determination of C_{org} in the soils by the wet combustion method using $Cr_2O_7^{2-}$. A study was conducted to determine an accurate and reliable method for estimation of C_{org} in acid sulphate soils in Malaysia containing variable amounts of pyrite. Some of the established methods of carbon (C) determination were tested against Carbon Determinator (Leco IR-312) which was regarded as the standard method. It was found that the interference of pyrite in the determination of C in acid sulphate soils by wet combustion was minimal. The total oxidation procedure was found to be the most reliable and accurate method for determination of C_{org} in acid sulphate soils in the absence of Carbon Determinator. The Walkley-Black method underestimated, while the loss on ignition method overestimated the C_{org} content in the soils.

INTRODUCTION

Carbon (C) is an important chemical constituent of organic matter in a soil. Organic matter has the ability to reduce Al toxicity in the soil via chelation mechanism. It has to be estimated accurately in order to assess its contribution to the reduction of Al toxicity. However, C in the soil can exist as a chemical component of organic matter or as impurities in inorganic compounds. In most soils of the humid tropics, C_{org} is the dominant form. On the other hand, C_{org} is found almost exclusively in association with calcite and/or dolomite in the soils of the arid and semi-arid regions (Nelson and Sommers 1982; Yeomans and Bremner 1991).

Soils in the aquatic moisture regime, where acid sulphate soils occur, contain variable amounts of organic matter. These acid sulphate soils are often characterized by the presence of pyrite in the reduced zone of the profiles. Carbonate is absent in the active acid sulphate soils of Malaysia (Shamshuddin and Auxtero 1991; Auxtero *et al.* 1991), suggesting that C in the soils is present exclusively as a component of organic compounds. Hence, C_{org} in the soils can be approximated from determination of total C. Organic matter can then be calculated from the total C.

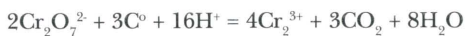
Total C in highly weathered soils under well drained conditions can be determined accurately by dry combustion using Leco Carbon

Determinator (Yeomans and Bremner 1991). Currently, C_{org} in such soils is determined by reduction of $Cr_2O_7^{2-}$ by organic C compounds and subsequent determination of unreduced $Cr_2O_7^{2-}$ by oxido-reduction titration with Fe^{2+} (Nelson and Sommers 1982). However, this procedure may not be accurate for determination of C in the soils containing substantial amounts of pyrite (FeS_2). This is because $Cr_2O_7^{2-}$ reacts with pyrite (Dent 1986), leading to an overestimation of the value of C. Willet and Beech (1987) found that overestimation of C_{org} occurred when pyrite content exceeded 0.29%. Acid sulphate soils in Malaysia (Shamshuddin and Auxtero 1991) and elsewhere in the world (Dent 1986) contain appreciable amounts of pyrite. Thus, it appears impractical to determine C in acid sulphate soils by the wet combustion method using $Cr_2O_7^{2-}$. The objective of this paper was to determine the accuracy of the wet combustion method using $Cr_2O_7^{2-}$ or any other available methods in the estimation of C_{org} in acid sulphate soils.

MATERIALS AND METHODS

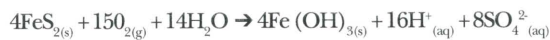
Theoretical Consideration

Organic matter in soils (Schollenburger 1927) may be oxidized by treatment with a hot mixture of $Cr_2O_7^{2-}$ and H_2SO_4 according to the equation:



After reaction, the excess $Cr_2O_7^{2-}$ is titrated with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and $Cr_2O_7^{2-}$ reduced during the reaction with soil is assumed to be equivalent to the organic C in the sample (Nelson and Sommers 1982).

Oxidation of pyrite (Retsema and Groenenberg 1993) in acid sulphate soils resulting from exposure to the atmosphere through drainage or otherwise can be visualized as follows:



This pyrite can be similarly oxidized if it comes into contact with $Cr_2O_7^{2-}$. Hence, $Cr_2O_7^{2-}$ does not only oxidize C_{org} but also pyrite in the acid sulphate soils. The assumption that the excess $Cr_2O_7^{2-}$ titrated with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is equivalent to the C_{org} is no longer valid.

The Soils

Soils for the study were acid sulphate soils sampled in Muar, Pontian and Serkat (Johor), Kuantan (Pahang) and Kuala Linggi (Melaka); these are important acid sulphate areas in Peninsular Malaysia. Appropriate samples were stored at 4°C to be used for incubation study and for determination of pyrite content. Other samples were air-dried and ground to pass through a 2-mm sieve. The pH, carbon and pyrite content are given in Table 1.

TABLE 1.
The pH, C and pyrite content in the Cg horizons of Sedu, Linau, IPRS and Jawa soils

Soils	Location	pH (H_2O , 1:1)	Carbon (%)	Pyrite (%)
Sedu	Kuala Linggi	1.9	7.49	0.60
Linau	Kuantan	3.1	5.87	0.02
IPRS	Pontian	2.2	4.19	0.12
Jawa	Serkat	2.4	4.33	0.26

Methods

a) Determination of Pyrite

Pyrite in the soils was determined according to a procedure proposed by Haering *et al.* (1989). Samples for this analysis were first dried under vacuum to avoid oxidation of pyrite before the determination.

b) Incubation Experiment

The samples from the Cg horizon of the Jawa and IPRS soils were incubated for 180 d. The samples were kept under moist conditions at room temperature by spraying with distilled water at appropriate times. Carbon in the soils was determined every 30 d by wet combustion using $Cr_2O_7^{2-}$ (total oxidation).

c) Carbon Analysis

Leco IR - 312. Carbon in the soils was first determined by the Leco IR - 312 Carbon Determinator. In this analysis, a sample was weighed in a crucible on a pan balance built into the measurement unit. About 0.1 g sample was needed for each determination. The crucible was transferred to the induction furnace, and the sample was burnt

off by O_2 to produce CO_2 at temperature around $2000^\circ C$. The C was detected by infrared. This represents total C in the soils. This method is regarded as the standard method for determining C in this study, and is referred to as Leco.

Wet combustion using $Cr_2O_7^{2-}$. C_{org} was also determined by total oxidation using $Cr_2O_7^{2-}$ by a modified Mebius procedure and by Walkley-Black method (Nelson and Sommers 1982). These are referred to as TO and WB, respectively.

A modified version of the wet oxidation method followed by colorimetric determination of C_{org} in acid sulphate soils was adopted. This method made use of Al_2O_3 equal in weight to the soil used. The Al_2O_3 was expected to reduce the oxidation of pyrite by dichromate ion (Frendorf *et al.* 1993). Determination of C_{org} was carried out with Al_2O_3 (+) or without Al_2O_3 (-).

Loss on Ignition. Carbon in the soils was finally determined by the method of loss on ignition. A 10 g oven dry soil sample was placed in a muffle furnace for 16 h at $375^\circ C$. The loss in weight was determined, and was attributable to the oxidation of organic matter (Dent 1986). C_{org} in the soil sample was estimated by dividing the organic matter so obtained by 1.724. Note that pyrite in the soil did not interfere with the determination as it only undergoes endothermic reaction at $450 - 650^\circ C$ (De Coninck 1978). This method is referred to as LI.

RESULTS AND DISCUSSION

The appearance of yellowish mottles after 30 d of incubation showed that the soils taken from the Cg horizon of acid soil profiles contained pyrite. The yellowish mottles were jarosite formed by the oxidation of pyrite. The pyrite content of the study soils ranged from 0.02 to 0.60% (Table 1).

The C content in the IPRS and Jawa soils was 4.19 and 4.33%, respectively (Table 1). The C content in both soils decreased linearly as the time of incubation increased (Fig. 1). The decrease in the C content was presumably due to the loss of organic matter resulting from its mineralization during the 180 d incubation. Some pyrite could have been oxidized to jarosite during the oxidation period. The decrease in C value with time of incubation could also be due to the smaller contribution from the oxidation of pyrite. It appeared that pyrite did interfere with the determination of C by wet combustion using $Cr_2O_7^{2-}$.

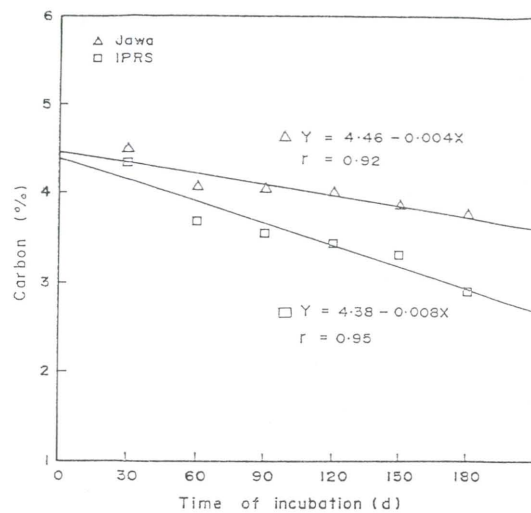


Fig 1: Reduction of C values in relation to time of incubation

The extent to which pyrite interfered with the determination of C by wet combustion using $Cr_2O_7^{2-}$ is illustrated in Fig. 2. The total oxidation Mebius procedure gave C values closest to the values determined by the standard method (Leco), giving a linear regression line of:

$$Y = 0.106 + 0.961X, \quad r = 0.994, \quad P < 0.01$$

There was a good agreement between C determined by total oxidation and that by Leco. Thus, the total oxidation Mebius method can be used accurately for determination of C in acid sulfate soils containing pyrite. The contribution of pyrite oxidation to the overall result of C determination by wet combustion appeared to be small.

The Walkley-Black method estimated lower values of C than the Leco method. On the other hand, the loss on ignition method recorded higher values than the Leco method. The higher values recorded by the loss on ignition method could be due to dehydration and/or dehydroxylation of minerals in the soil when it was heated to $375^\circ C$.

The C content determined by the loss on ignition was higher than that determined by the total oxidation or Walkley-Black method (Table 2). As expected, the C content determined by the total oxidation was higher than that determined by the Walkley-Black method. The modified Walkley-Black method through digestion with or without Al_2O_3 gave consistently lower C values

than the Leco method. The regression equations relating the C values determined by both methods are given in Table 2.

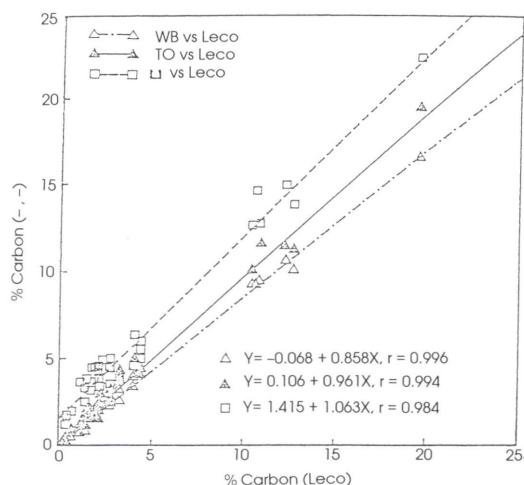


Fig 2: Carbon content determined by normal methods as compared to that by the standard method

TABLE 2

Linear relationship between C_{org} determined by total oxidation (TO), loss on ignition (LI), Walkley-Black (WB), Walkley-Black through digestion with $Al_2O_3(+)$ and without $Al_2O_3(-)$

Parameter	Equation	r(P < 0.01)
LI vs TO	$Y = 1.39 + 1.09X$	0.975
LI vs WB	$Y = 1.56 + 1.23X$	0.979
TO vs WB	$Y = 0.19 + 1.12X$	0.994
$Al_2O_3(-)$ vs Leco	$Y = -0.19 + 0.93X$	0.997
$Al_2O_3(+)$ vs Leco	$Y = -0.28 + 0.91X$	0.994

CONCLUSION

Pyrite appears to interfere with determination of C in acid sulphate soils by wet combustion using $Cr_2O_7^{2-}$, but its overall contribution is minimal. The total oxidation method gives the closest estimate to the actual C content in the soils. Total oxidation Mebius method is, therefore, suitable for C determination in acid sulphate soils containing pyrite in the absence of Carbon Determinator.

ACKNOWLEDGEMENT

The authors would like to record their gratitude to Universiti Pertanian Malaysia and the National Council for Scientific Research and Development and Petronas for financial and technical support in the conduct of the study.

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(Received 24 May 1992)