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Professional paper

COMPARATIVE COST ANALYSIS OF SOIL CARBON DETERMINATION USING TOC ANALYZER *vs.* WALKLEY-BLACK METHOD

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Abstract

Soil carbon measurement is critical for understanding soil health, fertility, and the role of soils in global carbon cycling and climate change mitigation. Two widely used methods for determining soil organic carbon (SOC) are the Walkley-Black method and the use of Total Organic Carbon (TOC) analysers. Each method has unique strengths and limitations, making them suitable for different applications depending on accuracy, cost, and available resources. This study compares the costs associated with both techniques, including capital investment, consumables, labour, maintenance, and waste disposal. Moreover, the quality assurance comparative analyses have been applied as well, assuming the basic reference criteria, such as: precision, accuracy and uncertainty of the measurements. Data from multiple laboratories and sample scales are used to develop a comprehensive cost model. The analysis highlights the trade-offs between precision, scalability, and cost-effectiveness, offering insights for selecting the most suitable method for different applications.

Key words: *soil, carbon, TOC analyser, Walkley-Black method, cost-effective method.*

INTRODUCTION

Carbon in soil is crucial for maintaining soil health, fertility, and overall ecosystem stability. It primarily exists in the form of soil organic carbon (SOC), which originates from decomposed plant and animal materials (Bronick & Lal, 2005; Bienes et al., 2021). The importance of carbon in soil includes several key aspects, regarding: 1) soil structure and water retention, 2) nutrient supply, 3) microbial activity, 4) soil fertility and productivity and 5) carbon sequestration. Carbon improves soil structure by promoting the formation of aggregates, enhancing water-holding capacity, and reducing erosion (Qi et al., 2022). Organic matter rich in carbon provides a slow-release source of essential nutrients like nitrogen, phosphorus, and sulphur for plant growth (Ramesh et al., 2019; Bhattacharyya et al., 2022). Soil carbon supports diverse microbial communities that decompose organic matter, cycling nutrients back into forms that plants can absorb (Liang et al., 2017; Bhattacharyya et al., 2022). Higher carbon content is directly linked to increased soil fertility, which leads to better crop yields and sustainable agricultural practices (Merckx et al., 2001; Triberti et al., 2016; Coonan et al., 2020; Javed et al., 2022).

An accurate and cost-effective soil carbon analysis is crucial for sustainable agricultural management, climate change mitigation, and environmental monitoring. SOC is a key indicator of soil fertility, water retention, and structure, influencing crop productivity and ecosystem services (Paustian et al., 2019). Additionally, soil acts as a significant carbon sink, playing a vital role in regulating atmospheric carbon dioxide levels (Acharya et al., 2022).

Soil organic carbon measurements are essential for evaluating soil health, guiding fertilization strategies, and improving land productivity (Paustian et al., 2019). Accurate data is necessary for quantifying carbon storage in soils, informing climate policies, and participating in carbon credit markets (Andries et al., 2021). Carbon sequestration monitoring involves measuring and tracking the capture and storage of atmospheric carbon dioxide (CO_2) in natural or artificial reservoirs to mitigate climate change. The process primarily occurs in soils, forests, and oceans, with soil carbon sequestration being a critical component for sustainable agriculture and land management. Accurate monitoring is essential for evaluating the effectiveness of sequestration practices and ensuring compliance with environmental policies and carbon credit systems. Tracking carbon sequestration contributes to understanding soil fertility, water retention, and ecosystem stability.

Moreover, reliable carbon measurements support research on global carbon cycles and the development of sustainable land use policies. Monitoring allows for accurate accounting of CO_2 removed from the atmosphere, supporting efforts to reduce global warming. Reliable data is necessary for trading carbon credits and verifying offsets in voluntary and regulated carbon markets. Data-driven insights help in formulating and adjusting policies aimed at reducing greenhouse gas emissions (Bibri et al., 2020; Luo et al., 2024). However, agriculture is an economic sector that requires large financial investments. Accordingly, not every farmer is financially able to monitor the carbon content. A general drawback is of course the availability of cost-effective but precise analyses. Cost-effective methods enable widespread soil testing, especially for large-scale agricultural operations and research projects (Heil et al., 2022). Lowering the cost of analysis allows better use of limited resources, enhancing monitoring frequency and geographic coverage. Affordable testing methods democratize access to soil health information for farmers, smallholder agriculturalists, and resource-limited regions (Bachmann et al., 2022).

Soil carbon is highly variable across locations and depths, primarily depended from the lithogenic and paedogenic environment (Lorenz et al., 2018; Lal et al., 2021). Soil carbon determination traditionally relies on dry combustion methods which require expensive equipment and high operational costs (Hammes et al., 2007; Chatterjee et al., 2009). Consequently, cost-effective alternatives are needed to facilitate broader soil carbon monitoring, especially in resource-limited settings. Techniques like the Walkley-Black method and Total Organic Carbon (TOC) analysers are frequently used to measure soil organic carbon (SOC) (Schumacher, 2002). In such research, it is necessary to make an assessment in balancing cost and accuracy of the selected methodology. Methods such as the Walkley-Black method and TOC analysers vary in cost, accuracy, and ease of use. Efficient selection of techniques based on project needs can optimize both budget and data reliability. Emerging technologies and hybrid approach further improve cost-efficiency without compromising accuracy.

Precise and accurate measurement of SOC is essential for sustainable land management and climate mitigation strategies. While the Walkley-Black method is a traditional chemical approach, the TOC analyser represents a modern, automated solution. Both methods have distinct cost structures influenced by equipment, consumables, labour, and maintenance.

The main goal of this paper is to introduce the comparative analysis for both soil carbon analysis methods, thus to: (1) evaluate the accuracy, based on the available published data (2) analyse cost and time efficiency, (3) recommend best practices for implementation. This paper aims to provide a detailed cost comparison, aiding decision-makers in selecting cost-efficient analytical approaches for various contexts.

MATERIAL AND METHODS

A separate evaluation of both methods was performed through a review of available data from manufacturers' technical specifications and available research articles for the application and validation of the methods.

Walkley-Black method

The Walkley-Black method, based on dichromate oxidation, is a standard chemical analysis technique, but its implementation cost can be significant depending on various factors. This study aims to develop a predictive cost model to estimate expenses associated with using this method, considering reagent consumption, labour, equipment, and waste management. It is a wet combustion method involving the oxidation of organic matter using potassium dichromate ($K_2Cr_2O_7$) in a sulfuric acid (H_2SO_4) medium. The methods principle is based on follow: the organic carbon in the soil is oxidized by potassium dichromate and concentrated sulfuric acid (Jha et al., 2014). The reaction generates heat, aiding the oxidation process. Excess dichromate that does not react with the organic matter is back-titrated with ferrous sulphate or ferrous ammonium sulphate to determine the amount of oxidant consumed. The analytical procedure includes: a known weight of soil (usually 0.5 to 1 g) is mixed with 1 N potassium dichromate solution. Then, the concentrated sulfuric acid is added, and the mixture is gently swirled to ensure complete reaction. The solution is left to cool. Excess dichromate is titrated with 0.5 N ferrous sulphate solution using an appropriate indicator (usually diphenylamine or orthophenanthroline). The organic carbon content is calculated based on the amount of dichromate reduced (Tóth et al., 2006; Stevens et al., 2008; Wight et al., 2016).

Cost components included in the methodology are given as follow:

- Chemicals: Potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4) and ferrous sulphate ($FeSO_4$) for titration;
- Labor: Time required for sample preparation, titration, and calculations;
- Equipment and consumables: Glassware (burettes, pipettes, flasks), balances and fume hoods;
- Waste Disposal: Costs associated with disposing of hazardous chromium-containing waste.

According to the set of variables for determining the real costs of applying the method, the following mathematical operation can be performed:

$$\boldsymbol{Total\ Cost} = C_{chemicals} + C_{labor} + C_{equipment} + C_{waste}$$

Where:

$$C_{chemicals} = \frac{Price\ per\ unit\ reagent \times Quantity\ used\ per\ sample}{Sample\ count}$$

$$C_{labor} = \frac{Hourly\ wage \times Processing\ time\ per\ sample}{Sample\ count}$$

$$C_{equipment} = depends\ on\ the\ depreciation\ over\ the\ equipment's\ lifespan$$

$$C_{waste} = depends\ on\ local\ disposal\ fees\ for\ hazardous\ materials$$

Soil Carbon Analysis with TOC Analyzer

Soil carbon analysis using a TOC analyser is commonly used analytical technique for monitoring the carbon cycle in agricultural land. This technique measures the amount of organic carbon in a soil sample, providing insights into the organic matter content (Qian & Mopper, 1996). The main key steps in TOC-based soil carbon analysis sample preparation, are given as follow: soil sample is submitted to air-dry process to remove the moisture. Sample is than ground and sieved in order to achieve a uniform particle size, typically less than 2 mm. Furthermore, for distinguishing between total carbon (TC) and inorganic carbon (IC), pretreatment with acid (e.g., HCl) may be performed in order to remove inorganic carbon content (Bisutti et al., 2004; Sleutel et al., 2007).

The principle of analysis is based on combustion or chemical oxidation of the sample at high temperatures to release carbon dioxide. The released CO_2 is detected and quantified using infrared spectroscopy. TOC values can also be used to estimate soil organic matter (SOM), via a conversion factor (e.g., SOM ≈ TOC × 1.72) (Sleutel et al., 2007).

According to the set of variables for determining the real costs of applying the method, the following mathematical operation can be performed:

$$\textbf{Total Cost} = \frac{C_{capital}}{L \times S} + C_{consumables} + C_{maintenance} + C_{labor} + C_{energy}$$

Where:

$C_{capital} = purchase\ cost\ of\ the\ TOC$

$L = lifespan\ of\ the\ equipment\ in\ years$

$S = numberof\ samples\ analyzed\ per\ year$

$C_{onsumables} = cost\ of\ reagents\ and\ consumables\ per\ sample$

$C_{maintenance} = annual\ maintenance\ cost$

$C_{labor} = cost\ of\ operator\ time\ per\ sample$

$C_{energy} = energy\ cost\ per\ sample$

$C_{waste} = depends\ on\ local\ disposal\ fees\ for\ hazardous\ materials$

Data collection and model application

Data were collected from laboratory equipment vendors, consumable suppliers, and maintenance service providers. The model was applied to estimate costs for analysing sample sizes ranging from 10 to 100. The prediction variable for the increment of the sample number, especially for cases above 500. Data collection for the prices for both methods vary widely based on the type, features, and region. Prices evaluation for TOC analysers has been conducted covering available online data from the producers located in Europe, USA and China. The selection was based on three dominant producers, ranged the technology scale at three levels: prices for 1) Overview basic/entry-level models; 2) Mid-range models: main application for industrial and environmental monitoring applications; 3) High-end/Advanced models: mainly for research applications. The data collection for Walkley-Black method as traditional chemical analysis technique, involved evaluating factors: reagents, equipment and scalability at the one mid-range level, occupying producers from Europe, USA and China. The range of the applicability for Walkley-Black method was extracted as follow: 1) Low-throughput laboratories: with significant labour costs; 2) High-throughput laboratories: economies of scale in reagent and labour use.

RESULTS AND DISCUSSION

This paper aims to provide a detailed cost comparison, aiding decision-makers in selecting cost-efficient analytical approaches for various contexts. According to separate mathematical definitions for the total costs per method, critical variables that significantly affect the analytical processes are extracted, including satisfactory accuracy, precision and reproducibility in the application of the methods. Cost components for both methods are extracted into: a) Equipment and capital costs: TOC analyser purchase vs. glassware and titration equipment for Walkley-Black; b) Consumables: oxygen gas and reagents for TOC; dichromate, sulfuric acid, and ferrous sulphate for Walkley-Black; c) Labor: time for sample preparation, analysis, and cleanup; d) Maintenance and repairs: service contracts for TOC vs. routine glassware replacement. e) Waste management: disposal of hazardous chromium waste for Walkley-Black method. Cost variables are defined for each method based on actual data from equipment manufacturers, chemical suppliers, and laboratory operations (Table 1). The representative sample was given for average of samples number of 100, minimum two operators per methods (for the labor cost) and average of 10 kg of waste.

According to the set of variables available for the both analytical methods, we are proposing a model for determining the real costs for comparative analysis of both methods. The following mathematical operation can be performed:

$$\boldsymbol{Total\ Cost_{method}} = C_{capital} + C_{consumables} + C_{maintenance} + C_{labor} + C_{waste}$$

Where:

$$C_{capital} = C_{equipment} + C_{instalation} + C_{software} + C_{trainng\ per\ hour}$$

$$C_{consumables} = C_{chemicals} + C_{initial\ materials} + C_{reference\ standards}$$

$$C_{maintenance} = C_{maintence\ per\ hour} + C_{replaceable\ materials} + C_{reference\ standards}$$

$$C_{labor} = C_{operating\ per\ hour} \times N_{operators} \times N_{working\ hours}$$

$$C_{waste} = C_{disposal\ fee\ per\ Kg} \times N_{operating\ days} \times 10$$

To obtain the final values for the individual variables, they were divided by 100 to obtain the price per sample. High variability in prices per sample is obtained for a representative total sample of more than 500 samples.

Table 1. Cost breakdown per sample (average costs values are given as Euro per sample).

Component	**TOC analyser**	**Walkley-Black method**
Capital equipment	5.00	0.50
Consumables	6.50	2.00
Labor	2.00	4.00
Maintenance	1.00	0.30
Waste disposal	0.10	0.70
Total	**14.6**	**7.50**

Cost data for Walkley-Black method were gathered from laboratory suppliers, labour rates, and waste disposal services. Chemical costs accounted for 25% of total expenses. Labor represented the largest cost burden of 55%, while equipment, maintenance and waste disposal shared the remaining 20%. A decrease in per-sample cost was observed with increasing batch sizes due to labour efficiency and bulk chemical pricing.

For TOC analyser method capital cost depreciation accounted for 35% of the total cost. Consumables represented the largest share at 45%, including oxygen gas and combustion tubes. Labor and maintenance each contributed approximately 20%. Costs decreased as the number of samples increased, showing economies of scale. Bulk purchasing of consumables and streamlined sample processing improved cost efficiency. The predictive model enables laboratories and research institutions to estimate TOC analysis costs accurately. Strategies to reduce costs include maximizing equipment utilization, negotiating bulk pricing for consumables, and adhering to preventive maintenance schedules.

Cost behaviour across sample sizes

The costs associated with both methods generally include: 1) Fixed costs (unrelated to sample size): and 2) Variable costs (related to sample size). The ranged of the fixed cost for TOC analysers range from 20,000 to 80,000 Euros, Walkley-Black method range from 500 to 2000 Euros. Significant variation occurs for the variable cost (usually form 10-30% from the initial fixed cost). Costs per sample for TOC decrease with larger batch sizes due to capital cost amortization, whereas Walkley-Black remains relatively constant due to low capital investment (Table 1). Precision vs. cost TOC analysers offer superior precision and automation but require higher upfront investment and specialized maintenance. The Walkley-Black method is cost-effective for small-scale or low-budget projects but involves chemical hazards and manual labour. The Walkley-Black method generates hazardous waste requiring proper disposal, adding environmental costs not directly reflected in financial expenses. This comparative analysis demonstrates that TOC analysers are cost-effective for large-scale, high-precision applications, while the Walkley-Black method remains suitable for smaller, budget-limited projects. For low-throughput labs, the Walkley-Black method is cost-effective, but labour and safety concerns can add hidden costs. For high-throughput labs, a TOC analyser becomes more economical over time, especially when labour and reagent savings are considered.

Comparative analysis based on quality assurance (QA) of the methods

A comparative analysis based on the accuracy, precision and measurement uncertainty of TOC analysers and the Walkley-Black (WB) method evaluates their accuracy, reliability, and efficiency in measuring SOC content. The evaluation is conducted on the available data already published (Table 2). Regarding the precision and accuracy, TOC analyser provides highly precise and repeatable measurements by directly measuring carbon content using combustion and infrared detection. It minimizes human error and is suitable for low and high carbon concentrations, which results with lower mean values for standard deviation and variance (CV). Walkley-Black method as traditional chemical method involving increased time efficiency, export satisfactory precision, similar as TOC analyser. In addition to, WB method, demands time-consuming, requiring manual steps and careful titration, increasing the data inputs in the uncertainty indicator (Table 2).

Table 2. Data summary of comparative analysis of published improvements in QA for TOC analyser and WB method.

Sensitivity check	Improvement	TOC analyser	WB method	Data referenced from the past 2 decades:
Precision	MAE (%)	1.70	1.65	Weil et al., 2003; Bisutti, et al., 2004; Tóth et al., 2006; Sleutel et al., 2007, Stevens et al., 2008; Chatterjee et al., 2009; Petrokofsky et al., 2012; Da Silva Dias et al., 2013; Jha et al., 2014; Johns et al., 2015; Wight et al., 2016; Vitti et al., 2016; Davis et al., 2017; Nayak et al., 2019; Van Der Voort et al., 2023; Dupla et al., 2024.
Accuracy	SD (%)	0.45	0.52	
Uncertainty	CV (%)	26.5	32.5	

*MAE - Mean Absolute Error, SD - Standard Deviations, CV – Coefficient of Variation

Measurements for soil carbon using TOC analyser provides high accuracy, referred with values of analytical recovery in the range from 86 to 112%, as it uses direct measurement of organic carbon through combustion and detection of CO_2. The application of this methodology eliminates human error associated with manual titration. Results are typically more reproducible and reliable for a wide range of sample types. TOC Analyzer offers superior precision due to automated, standardized procedures. Moreover, repeatability is enhanced by advanced instrumentation with minimal human intervention.

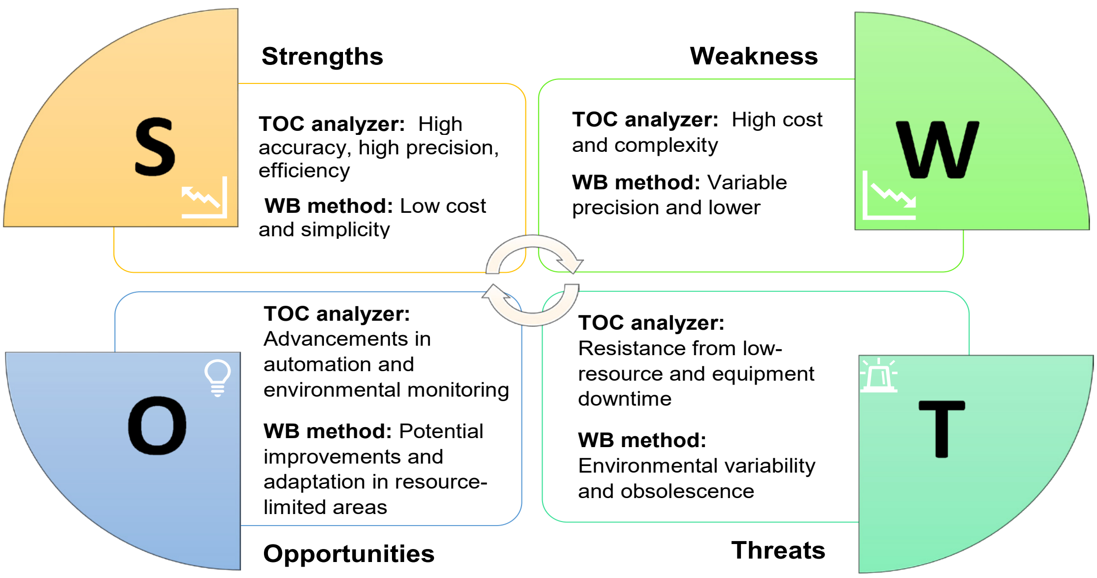
Walkley-Black method: Historically reliable but tends to underestimate TOC by 10-30% since it does not oxidize all organic carbon. Accuracy depends on the assumption of a fixed efficiency factor (often higher than 77%). The Walkley-Black method is often referenced for its susceptibility to analytical risks, including procedural errors and reagent quality concerns. Precision can vary based on the skill of the operator and consistency in handling reagents. Manual titration steps introduce higher variability of the reproducibility and repeatability of the measurements. The improvement of the reduced risk is conducted through the process of validation of the analytical procedure.

SWOT analysis

SWOT analysis summarizes key factors for the application of both methodologies (TOC and WB) for quantification of soil carbon content (Figure 1). Key indicators of both techniques were extracted using SWOT analysis. High accuracy of TOC analysers relays on direct combustion method, which ensures reliable carbon quantification. Automated process minimizes human error, resulting with incompatible high precision. Moreover, this methodology is suitable for high-throughput and diverse sample types. On the other side, the implementation of TOC analyser demands high initial investment and maintenance expenses. Furthermore, it requires technical expertise and specialized personnel. Thus, this methodology encounters resistance in low-resource settings due to its high cost. Routine monitoring programs often face equipment downtime, leading to an increased risk of analysis delays caused by maintenance requirements.

Walkley-Black method as traditional analytical procedure remains as the most economical and widely accessible methodology for soil carbon determination. This method requires only basic laboratory equipment and basic analytical skills. Moreover, is adaptable for routine analyses. Some laboratories refer to lower accuracy, due to the underestimates carbon content. The analytical recovery of approximately 70-80% results due to the partial oxidation of the organic compounds. However, this analytical risk can be decreased with validation process and implementation of control samples (reference materials or standard addition method). Mostly, results depend on operator skill and titration consistency. Thus, dominant opportunity for the WB application lies in its adaptation for use in resource-limited areas.

Figure 1. SWOT analysis TOC analyser vs. WB method.



CONCLUDING REMARKS

Investing in accurate, cost-effective soil carbon analysis supports sustainable land management, enhances climate resilience, and contributes to global efforts to combat climate change. Improving accessibility and affordability of reliable methods is key to maximizing environmental and economic benefits. Effective carbon sequestration monitoring is vital for climate action, sustainable agriculture, and economic incentives through carbon trading. Investing in reliable, cost-effective, and scalable monitoring systems will enhance global efforts to manage carbon and mitigate climate change.

Selection should be based on project scale, precision requirements, and available resources. The predictive cost model enables better financial planning for laboratories and research institutions. Cost per sample can be minimized by optimizing reagent use, training staff for efficiency, and investing in durable equipment. The proposed cost model provides a robust tool for predicting expenses associated with the Walkley-Black method. It supports strategic decision-making for large-scale soil carbon analysis initiatives. The TOC Analyzer is superior in both accuracy and precision, making it the preferred method for critical applications, while the Walkley-Black method remains valuable for cost-effective, routine SOC analysis with acceptable precision.

The TOC Analyzer leads in precision and accuracy but is limited by cost and complexity, while the Walkley-Black Method is cost-effective but less reliable, offering unique advantages for field application.

To summarise, maintaining adequate carbon levels in soil is vital for soil health, sustainable agriculture, and environmental protection. Soils act as major carbon sinks, storing carbon and mitigating climate change by reducing atmospheric carbon dioxide levels.

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КОМПАРАТИВНА АНАЛИЗА НА ТРОШОЦИ ЗА ОПРЕДЕЛУВАЊЕ НА ЈАГЛЕРОДОТ ВО ПОЧВАТА СО КОРИСТЕЊЕ НА TOC АНАЛИЗАТОР *vs.* WALKLEY-BLACK МЕТОДОТ

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Резиме

Мерењето на јаглеродот во почвата е критично за разбирање на плодноста на почвата и улогата на почвите во глобалниот циклус на јаглерод, како и намалување на ефектите на климатските промени. Два широко користени методи за одредување на органски јаглерод во почвата (SOC) се методот Walkley-Black и употребата на анализатори за одредување на вкупен органски јаглерод (TOC). Секој метод има уникатни предности и ограничувања, што ги прави погодни за различни апликации во зависност од точноста, цената и расположливите ресурси. Оваа студија ги споредува трошоците поврзани со двете техники, вклучувајќи капитални инвестиции, потрошен материјал, работна сила, одржување и отстранување на отпадот. Дополнително, применети се и компаративните анализи за обезбедување квалитет, при што се претпоставуваат основните референтни критериуми, како што се: прецизност, точност на мерењата, како и мерната неодреденост. Податоците од повеќе производители, дистрибутери и лаборатории се користени за да се развие сеопфатен модел на трошоци и квалитет на анализа. Извршената анализа на податоци ги екстрахира зависностите помеѓу прецизноста, приспособливоста и економичноста, нудејќи увид во изборот на најсоодветен метод за различни апликации и услови на примена.

Клучни зборови: *почва, јаглерод, TOC анализатор, Walkley-Black метод, економична метода.*