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Comparative assessment of analytical methods for calcium carbonate determination in sands

Isabelle Joanne Viana Coelho Cesar[1]#, Victor Carlos Vital Cavalcanti[1], Mariana Ramos Chrusciak[1], Bruna de Carvalho Faria Lima Lopes[2]

Technical Note

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Abstract

Accurate quantification of calcium carbonate ($CaCO_3$) in soil is critical for geoenvironmental engineering, influencing soil stabilization, carbon sequestration, and climate-resilient design. This study compares four commonly used analytical methods—Loss on Ignition (LoI), Total Inorganic Carbon (TIC), X-Ray Diffraction (XRD), and a Calcium Carbonate Analyzer (CCA)—over $CaCO_3$ concentrations from 0.3% to 50%. Controlled sand samples with known carbonate contents were tested to assess each method's accuracy, precision, and reproducibility. Although LoI proves the most practical due to its simplicity and throughput, all methods face marked difficulties at low concentrations. Root Mean Square Error (RMSE) analysis shows that small discrepancies at low $CaCO_3$ levels can produce disproportionately large relative errors, obscuring actual measurement uncertainties. Factors such as sample representativeness, operator handling, and instrument resolution further amplify inconsistencies, emphasizing the need for more rigorous protocols. Crucially, none of the evaluated methods consistently captures very low $CaCO_3$ concentrations, posing significant challenges for soil carbon capture initiatives, regulatory compliance, and soil management practices. These findings highlight the urgent need to refine existing procedures or use alternative approaches to more accurately quantify $CaCO_3$ content at low levels, thereby enhancing confidence in research outcomes and applied engineering solutions.

1. Introduction

Calcium carbonate ($CaCO_3$) is widely recognized as a cornerstone in geoenvironmental engineering, influencing a range of soil properties including stiffness, strength, and carbon sequestration potential (Li et al., 2023; Washbourne et al., 2012). Over the past decades, $CaCO_3$ has been central to the design of soil stabilization projects (Dejong et al., 2013; El Mountassir et al., 2018) and to the development of innovative biogeochemical pathways for CO_2 capture (Manning & Renforth, 2013), underscoring its importance in both environmental and geotechnical applications. Despite considerable advancements in understanding $CaCO_3$ behaviour in soils, accurately quantifying low concentrations remains challenging (Clarkson et al., 2024), potentially introducing errors in carbon accounting, impeding the verification of geoengineering interventions, and complicating regulatory compliance efforts.

Numerous analytical methods have been developed for $CaCO_3$ determination, including Loss on Ignition (LoI), Total Inorganic Carbon (TIC) via dry combustion, X-Ray Diffraction (XRD), and pressure calcimetry (commonly referred to as the calcimetric method – here referred as Calcium Carbonate Analyser - CCA). Each method offers unique strengths but also faces specific limitations, particularly when $CaCO_3$ concentrations are low. For instance, CCA is valued for its simplicity and cost-effectiveness, yet it often exhibits reduced precision below certain $CaCO_3$ thresholds due to organic matter interference and limited instrumental sensitivity (Cantera & Ozán, 2022). XRD enables mineral-specific quantification, but it can produce inaccuracies when overlapping diffraction peaks or water loss in clay minerals obscure the carbonate signature (Xiao et al., 2023). LoI, which is straightforward and relatively inexpensive, may overestimate $CaCO_3$ in low-carbonate sediments owing to the partial decomposition of non-carbonate minerals at elevated temperatures (Fu et al., 2020).

#Corresponding author. E-mail address: isabellecesarufrr@gmail.com
[1]Universidade Federal de Roraima, Departamento de Engenharia Civil, Boa Vista, RR, Brasil.
[2]Newcastle University, School of Engineering, Newcastle upon Tyne, UK.

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Although modifications such as calibrating methods with soils spiked at known $CaCO_3$ levels have been proposed to enhance reproducibility (Heiri et al., 2001; Hoogsteen et al., 2015), these adjustments do not universally resolve the intrinsic shortcomings associated with each technique.

Comprehensive comparisons of these quantification methods, particularly at low $CaCO_3$ concentrations, remain scarce. Most published investigations concentrate on soils with high carbonate content or assess only a limited subset of approaches (Leogrande et al., 2021; Wang et al., 2012), limiting the broader applicability of their conclusions. This gap in the literature poses challenges for accurately assessing carbon sequestration, designing climate-resilient geoengineering strategies, and advancing sustainable soil management practices. Moreover, most comparative studies rely on real soils (Fu et al., 2020; Leogrande et al., 2021; Wang et al., 2012), where it is impossible to confirm the exact $CaCO_3$ concentration because each technique introduces an inherent measurement error. This core limitation complicates result validation and highlights the need for standardized methodologies to mitigate inaccuracies. Given that CO_2 capture estimates are highly sensitive to even minor errors, refining analytical procedures for low-$CaCO_3$ soils remains a pressing priority.

The present study addresses this gap by evaluating the performance of four commonly employed techniques—LoI, TIC, XRD, and CCA - across a range of $CaCO_3$ concentrations (0.3% to 50%) under controlled conditions. By systematically comparing these methods against known benchmarks, this work examines the respective accuracies, precisions, and limitations of current practices. The findings highlight the impacts of measurement uncertainty on carbon accounting and geoenvironmental applications, with particular emphasis on low-$CaCO_3$ soils that are prevalent in many engineered and natural environments. The results are intended to guide researchers and practitioners in selecting and refining analytical methodologies that align with contemporary needs in geoenvironmental engineering, including improved soil stabilization designs, robust carbon sequestration initiatives, and refined climate change mitigation strategies.

2. Materials and methods

Samples of pure quartz sand were prepared with varying $CaCO_3$ contents of 50%, 9.2%, 4.8%, 2%, 1%, and 0.3% by mass. These percentages were specifically chosen to cover a wide practical range, emphasizing lower concentrations due to their analytical challenges and critical knowledge gap identified in the literature. For each concentration, 3 replicates were prepared, except for the XRD analysis, where duplicates were prepared for the 50% and 0.3% samples only. To ensure accurate preparation, 2g of sand were used for most samples, with the appropriate mass of $CaCO_3$ (ACS reagent, ≥99.0%, powder) added. For the 0.3% samples, 5g of sand were used to avoid measurement errors due to the small quantity of $CaCO_3$ required. Before mixing sand and $CaCO_3$, both materials were dried at 40°C (for Total Inorganic Carbon – TIC test) and 105°C (all other tests), then the mix was ground using a pestle and mortar. The prepared samples were subsequently used for testing: approximately 2g for LoI, except for the 0.3% sample where 5g were used; around 0.15g for TIC; around 2g for XRD; and 1g for CCA, with an additional 2g sample (5g for 0.3%) for CCA to evaluate the influence of sample size.

For the LoI method, dried samples were placed in a furnace at 550°C for 5 hours, and then returned to the furnace at 950°C for an additional 3 hours before being weighed, following the procedure outlined by Heiri et al. (2001). To calculate the percentage of $CaCO_3$, it was assumed that the sample contained no organic matter and that all carbonates present were calcium carbonate, which is reasonable given the sample composition. The $CaCO_3$ percentage was calculated by taking the mass difference between the 105°C and 950°C measurements, dividing it by the mass at 105°C. This result was then divided by 0.44, which corresponds to the CO_2 fraction released during the thermal reaction (Dean, 1974).

For TIC, specimens were analysed using a Leco CS-244 Carbon Determinator, calibrated prior to the analysis of samples. The difference between the total carbon and organic carbon was divided by 12 to obtain the $CaCO_3$ content (Bernard et al., 2022).

In the XRD analysis, samples were backloaded into 16 mm sample holders, and a preliminary scan over a 2θ range of 5–100° was conducted to determine the crystallinity and appropriate scan settings. Phase identification was carried out using HighScore Plus software, with matching sequences performed using the PDF-2 database from the International Centre for Diffraction Data (ICDD) and the Crystallography Open Database (COD). Following phase identification, quantification was conducted via whole-pattern fitting using Rietveld refinement, with manual adjustments as necessary.

For CCA testing, procedures followed ASTM D4373-21 (ASTM, 2021). Two of the triplicated samples were analysed by placing 1g of specimen in a reaction cylinder with 20 mL of 1N HCl. The sealed reactor was shaken to ensure contact between the specimen and the acid, and after a 10-minute reaction, the pressure generated by CO_2 release was recorded. The pressure was then converted to $CaCO_3$ content using a previously established calibration curve. For the third sample in each set, a larger specimen (2g, or 5g for the 0.3% sample) was placed in the reaction cylinder, and the pressure reading was normalized by dividing the specimen mass before converting to $CaCO_3$ using the calibration curve.

3. Results and discussions

Figure 1 illustrates the correlation between the real $CaCO_3$ content and the average measured values obtained from the different analytical methods. As shown in Figure 1a, all methods underestimate the $CaCO_3$ content for the sample with 50% $CaCO_3$. Figure 1b zooms in on the lower concentration

range (0–10% $CaCO_3$), where greater variability among the methods becomes more apparent. In this range, LoI tends to overestimate the $CaCO_3$ content, while TIC consistently underestimates it, except for the 0.3% sample. XRD shows overestimation for samples with 9.2%, 4.8%, and 0.3% $CaCO_3$, but underestimates the others. CCA, on the other hand, overestimates the $CaCO_3$ content for the 9.2% and 1% samples, while underestimating the remaining concentrations. Additionally, the standard deviations for the replicated samples highlight that TIC generally have higher variability, while LoI and CCA produce more consistent results, although discrepancies still occur at lower concentrations.

The underestimation and overestimation observed across the methods can be attributed to several key factors. One issue is the representativeness of the specimens relative to the bulk sample. In methods like TIC, where only 0.15g of specimen is used, even slight variations in $CaCO_3$ distribution can lead to significant measurement discrepancies, especially at lower concentrations. In contrast, sample size might also influence the results, particularly for LoI, as highlighted by Heiri et al. (2001). To test this hypothesis, different amounts of pure $CaCO_3$ (2, 4, 6, 8, and 10g) were tested using the LoI method, with 100% $CaCO_3$ expected. However, the results averaged at 93.7%, with values ranging from 92.9% for the 10g sample to 96.6% for the 2g sample (Figure 2a), indicating that sample size might indeed impact the accuracy of the measurements. Conversely, for CCA, larger sample sizes yielded better results, with larger specimens producing more accurate measurements of $CaCO_3$ content (Figure 2b), suggesting improved representativeness in the CCA method when larger quantities are tested.

Instrument accuracy also contributes to variability, particularly in methods like CCA, where the manometer's coarse resolution (1 kPa per division) makes it challenging to detect small amounts of CO_2 release, leading to less precise results, especially at low $CaCO_3$ concentrations. Operator error is another significant factor, especially in CCA and LoI, where precision is required in both manometer readings and manual weighing. Even slight discrepancies, such as a 0.5 kPa difference in manometer readings or variations in the third decimal place of the sample weight, can result in notable errors when calculating $CaCO_3$ percentages.

Additionally, incomplete reactions may contribute to discrepancies, particularly in LoI. To investigate this, a 2g sample of pure $CaCO_3$ was sent for XRD analysis after LoI (LoI result = 96.6%). XRD confirmed that the sample contained 96.6% CaO and 3.4% $CaCO_3$, indicating incomplete reaction. Similarly, a 50% sand and 50% $CaCO_3$ sample analysed by XRD after LoI (LoI result = 48.5%) was found to contain 38.5% quartz (which should have been 50%), 0.8% $CaCO_3$, and 60.7% CaO, further suggesting incomplete decomposition of $CaCO_3$ and highlighting the limitations of XRD to quantify phases.

Despite these factors, the Root Mean Square Error (RMSE) values for the four methods—LoI, TIC, XRD, and CCA—are 0.778, 2.673, 0.989, and 1.229, respectively. These values indicate the average magnitude of error for each method when compared to the actual $CaCO_3$ content in the samples. At first glance, LoI and XRD exhibit lower RMSE values, suggesting better performance, while TIC shows the largest RMSE, indicating consistently higher deviations from the true values.

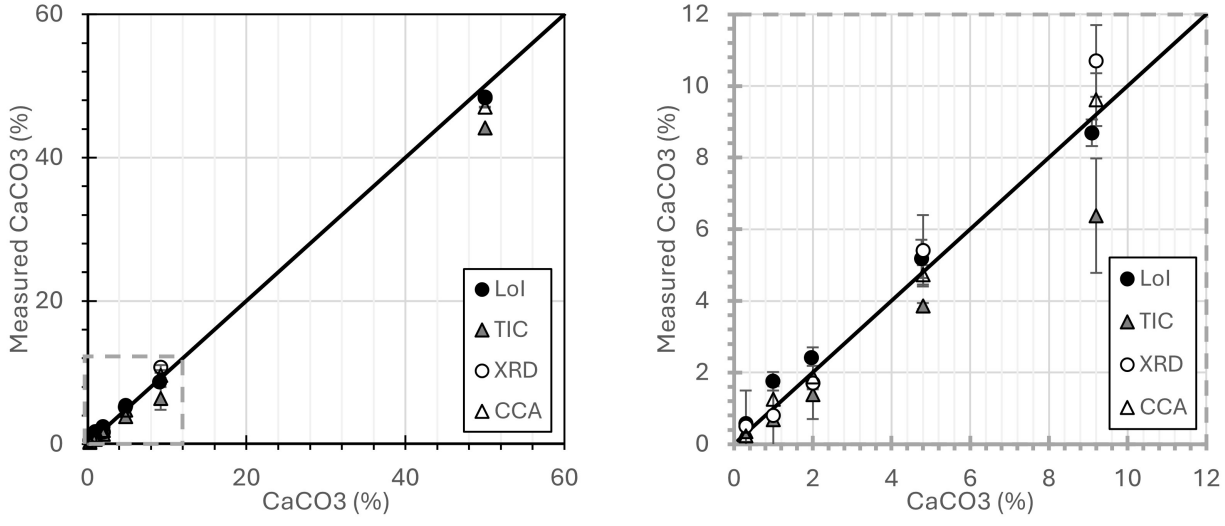
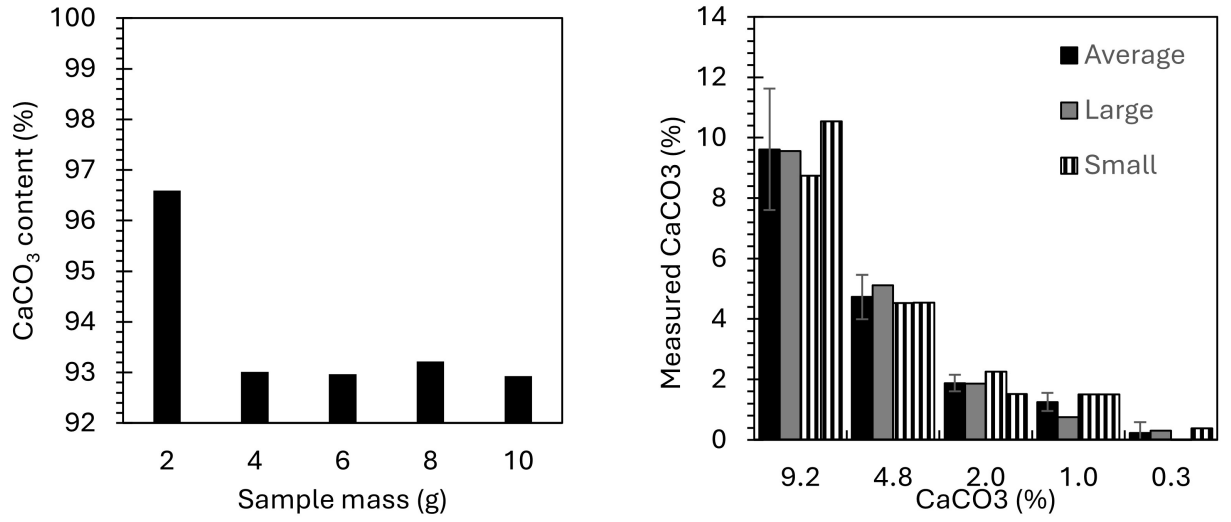


Figure 1. (a) Correlations between calcium carbonate content and average measured calcium carbonate content for different testing methods, (b) zoom on biaxial 10% calcium carbonate content, including standard deviation for replicated samples, where LoI: Loss on Ignition, TIC: Total Inorganic Carbon, XRD: X-Ray Diffraction, CCA: Calcium Carbonate Analyser.



(a) (b)

Figure 2. Sample size effect: (a) LoI and (b) CCA, where large refers to samples of 5g for 0.3% of $CaCO_3$ and 2g for all other concentrations and small for samples of 1g, as recommended by ASTM D4373-21 (ASTM, 2021).

However, interpreting these RMSE values presents certain challenges. For example, when examining the results for LoI at 0.3% and 50% $CaCO_3$ concentrations, significant differences become apparent. At 50% $CaCO_3$, the measured values are close to the actual content, with a maximum deviation of only 0.6%, resulting in accurate representation and contributing to the relatively low overall RMSE for LoI. In contrast, for the sample containing 0.3% $CaCO_3$, the measured values vary significantly, ranging from 0.5% to 0.7%. This creates large relative errors, with the highest measurement being more than double the actual content and even the lowest value reflecting an error of about 70%.

This example highlights the difficulty of interpreting RMSE in isolation. While LoI's overall RMSE of 0.778 appears small and suggests strong performance, this figure is largely influenced by the accurate measurements at higher concentrations, such as the 50% sample. Meanwhile, the large relative errors at lower concentrations, like the 0.3% sample, are masked by the averaging effect inherent in RMSE. Thus, although RMSE is a useful overall measure of error, it may not fully capture variability across different concentration ranges, particularly when small concentrations are critical.

4. Conclusions

This paper compared four commonly used analytical techniques for quantifying calcium carbonate ($CaCO_3$) in sand samples—Loss on Ignition (LoI), Total Inorganic Carbon (TIC), X-Ray Diffraction (XRD), and a Calcium Carbonate Analyzer (CCA)—with the overarching objective of assessing their accuracy and reliability across a broad range of concentrations. Through a series of controlled experiments spanning $CaCO_3$ contents from low (0.3%) to high (50%) levels, the investigation aimed to highlight the strengths and limitations of each method.

The results indicate that while LoI, TIC, XRD, and CCA can reliably estimate moderate-to-high $CaCO_3$ concentrations, all four methods exhibit notable performance challenges at low concentration levels. Although Root Mean Square Error (RMSE) analyses can reveal overall accuracy trends, small absolute differences at these lower concentrations tend to produce disproportionately large relative errors. Method selection therefore requires careful consideration of factors such as specimen size, operator handling, and instrument precision. Among the techniques tested, LoI emerged as the most advantageous due to its simplicity, minimal equipment requirements, and rapid sample throughput. However, findings confirm that none of the four methods can provide meaningful $CaCO_3$ measurements in very low concentration regimes, underscoring a persistent challenge for both researchers and practitioners. These insights reinforce the need for continued refinement of existing analytical protocols, particularly in the context of soil carbon sequestration assessments and the development of climate-resilient engineering solutions.

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Declaration of interest

The authors have no conflicts of interest to declare. All co-authors have observed and affirmed the contents of the paper and there is no financial interest to report.

Authors' contributions

Isabelle Joanne Viana Coelho Cesar: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft. Victor Carlos Vital Cavalcanti: investigation, methodology. Mariana Ramos Chrusciak: funding acquisition, project administration, supervision, validation. Bruna de Carvalho Faria Lima Lopes: conceptualization, formal analysis, funding acquisition, methodology, supervision, validation, writing – original draft.

Data availability

The datasets generated analysed in the course of the current study are available from the corresponding author upon request.

Declaration of use of generative artificial intelligence

This work was prepared without the assistance of any generative artificial intelligence (GenAI) tools or services. All aspects of the manuscript were developed solely by the authors, who take full responsibility for the content of this publication.

List of symbols and abbreviations

ACS	American Chemical Society
ASTM	American Society for Testing and Materials
$CaCO_3$	Calcium Carbonate
CCA	Calcium Carbonate Analyzer
CDRI	Coalition for Disaster Resilient Infrastructure
CNPq	Brazilian National Council for Scientific and Technological Development
COD	Crystallography Open Database
FNDCT	Brazilian National Fund for Scientific and Technological Development
HCl	Hydrochloric acid
ICDD	International Centre for Diffraction Data
ISPF ODA	International Science Partnerships Fund - Official Development Assistance
LoI	Loss on Ignition
MCTI	Brazilian Ministry of Science, Technology and Innovation
PIBIC-UFRR	Institutional program for scientific initiation scholarships, Universidade Federal de Roraima
RMSE	Root Mean Square Error
TIC	Total Inorganic Carbon
XRD	X-Ray Diffraction

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