A PROCEDURE FOR THE GRAVIMETRIC QUANTIFICATION OF TOTAL ORGANIC CARBON AND CARBONATES IN NATURAL ROCKS FOCUSED ON MINERAL AND COAL PROCESSING

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ABSTRACT. This paper presents a gravimetric method for the quantification of total organic carbon by ignition at 1100°C and carbonates by acid dissolution in rock samples containing coal. Two minerals (CM-1 and CM-2) and a sub-bituminous coal (SBC) were used in the study. The mineralogical characterization of the samples was performed by X-ray diffraction and scanning electron microscopy. This revealed the presence of calcite in samples CM-1 (20.4%) and CM-2 (74.7%), dolomite in CM-2 (0.7%), and graphite in sample SBC (42.6%). To eliminate carbonates, the samples were treated with 4 mol/L HCl, which allowed quantification. Results of the carbonate gravimetric quantification were compared with those obtained with a calcimeter. A significant difference was observed for the sample CM-2 (70.3% versus 63.4% by calcimetry, p-value = 0.0042). For the sample without carbonates, no differences were observed for loss on ignition without and with the acid treatment, so this is not necessary for this type of sample. A morphological study showed no significant surface change after acid treatment, but fracture of iron oxide particles was observed in CM-1 and CM-2 after heat treatment. In this study it was demonstrated that rock mineralogy is essential to correctly analyze organic and inorganic carbon content.

Keywords: *total organic carbon, gravimetry, carbonates, coal, mineralogy*

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INTRODUCTION

Total organic carbon (TOC) and inorganic carbon, the latter mainly as carbonates, are important chemical parameters for the characterization of samples such as soils, rocks, biomass, minerals, and some artificial materials [1–3]. They are also interesting parameters in water samples, since TOC in particular is a measure of the amount of organic matter present, which can be a toxicological problem in high amounts [4,5].

Although coal is not technically a mineral, it is considered as such in the context of coal processing. TOC quantification is especially important in solid samples containing coal because it is related to the potential as a fuel or its use as a carbon source, among others [6,7]. TOC and carbonates are essential determinations for coal beneficiation.

There are many analytical methods for determining TOC, the most commonly used being the instrumental method, the gravimetric method, and the volumetric method. Even within these, there is a wide variety of techniques. The instrumental method, commonly referred to as a TOC analyzer, is based on the exhaustive oxidation of organic matter and the detection of the CO_2 produced. When a catalyst is used, combustion requires a lower temperature. Chemical oxidation is commonly used with persulfate ion, which also occurs under heat-catalyzed conditions, radiation, or even both. While the instrumental method is preferable, such an analyzer is not always available in the laboratory. This forces the use of less expensive methods such as gravimetry, volumetry, or UV-vis molecular absorption spectrophotometry [8–10].

The gravimetric method for TOC is also a favorite, although it usually has some limitations. It is based on the oxidation of organic matter at an elevated temperature in a muffle, with quantification by the difference in weight before and after. It is therefore a gravimetric method by volatilization. The method actually measures the loss on ignition (LOI), which is related to the TOC by a proportionality factor. It is a method that looks simple, but in reality it is not, because the presence of carbonates and other volatile inorganic substances affects the result, so prior stages of removal of these are required. This brings up an important problem, which is that a unique procedure for the determination of TOC by gravimetry is not possible for all solid samples, but it is necessary to know the qualitative composition to establish a series of analytical steps to ensure a reliable TOC result. This is one of the main problems addressed in this work for natural samples with coal content [8–12]. Artificial intelligence has also reached TOC methods, for example, machine learning has been implemented for estimation based on mineralogical composition [2].

The volumetric redox method is based on wet oxidation with potassium dichromate and sulfuric acid. Part of the potassium dichromate is reduced to Cr^{3+}, while the excess is titrated with Fe^{2+}, usually from Mohr's salt or $FeSO_4$,

using ferroin as an indicator. The volumetric method has been carried out in various ways. This is the same basis as the spectrophotometric method for TOC, but the quantification is done by measuring the absorbance at the wavelength of the Cr^{3+} ion, which is close to 600 nm [9–11].

Carbonates, on the other hand, are potential interferences in the ignition-based TOC determination. This occurs because carbonates volatilize at a temperature lower than that at which the combustion of organic matter is completed. Therefore, it is important to quantify and eliminate them when determining TOC in mineral samples, where they are usually abundant [9,10].

Establishing an analytical method for TOC in mineral samples containing coal can be complicated because existing techniques are highly dependent on the chemical characteristics of the rock and the composition of mineral matrices is highly variable. This work presents a simple procedure for the quantification of TOC by the loss-on-ignition gravimetric method in mineral samples containing coal. The method takes into account the effect of carbonates and assumes their quantification as part of a step before TOC quantification. This procedure is mainly focused on the determination of TOC and carbonates in mineral and coal processing as a quantitative parameter in stages such as froth flotation.

RESULTS AND DISCUSSION

Physicochemical and mineralogical characterization of the samples

For this work, two carbonaceous mineral rocks (CM-1 and CM-2) from Mexican metallic sulfide processing mines were used. The third sample was a sub-bituminous coal (SBC) from a Mexican coal mine. The moisture and pH were determined for flotation studies and are presented in Table 1 [13,14].

Table 1. Properties of the mineral samples used in this work [13,14]

Sample	Moisture (%)	pH
CM-1	0.83	8.1
CM-2	0.33	7.8
SBC	0.58	7.0

CM: Mineral with coal content, SBC: Sub-bituminous coal

Figure 1a shows the XRD pattern of sample CM-1. It can be observed that the crystalline phases composing this sample are quartz, calcite, sphalerite, pyrite, and orthoclase. This means that this is a sample with a content of metallic sulfides and minerals of the silicate group. In addition, the presence of carbonate (calcite), which is the analytical objective of this work, is demonstrated by this
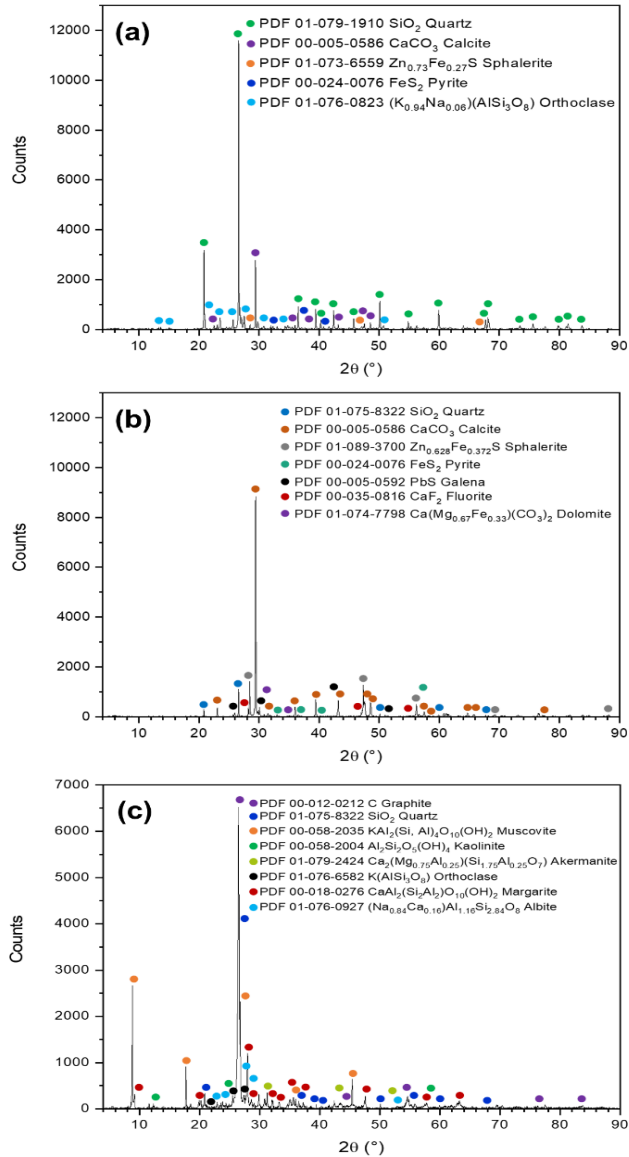
Figure 1. X-ray diffractograms: (a) Sample CM-1, (b) Sample CM-2, (c) Sample SBC.

technique. In the case of sample CM-2 (Figure 1b), something similar happens, but the variety of sulfide minerals is greater. Fluorite, calcite, and dolomite are also present. Calcite is the most common carbonate phase found in nature.

There are other $CaCO_3$ phases such as aragonite and vaterite, but they are less stable. Dolomite is a carbonate of calcium and magnesium formed by substitution in the limestone rock. In this case, dolomite phase has iron in the composition. In the case of the sample SBC (Figure 1c), there is no calcite phase or other carbonate, and there is a greater variety of silicates than in the previous samples. A graphite phase is observed in this sample, which is consistent with the fact that it is a coal.

Figure 2 shows the EDS spectra of different particles from sample CM-1. The morphological aspects of the samples will be discussed later in this paper. The three spectra show chemical elements associated with metallic sulfides, calcite, and silicates, showing in principle some agreement with the XRD results, although this is not entirely the case since it should be noted in Figure 2c
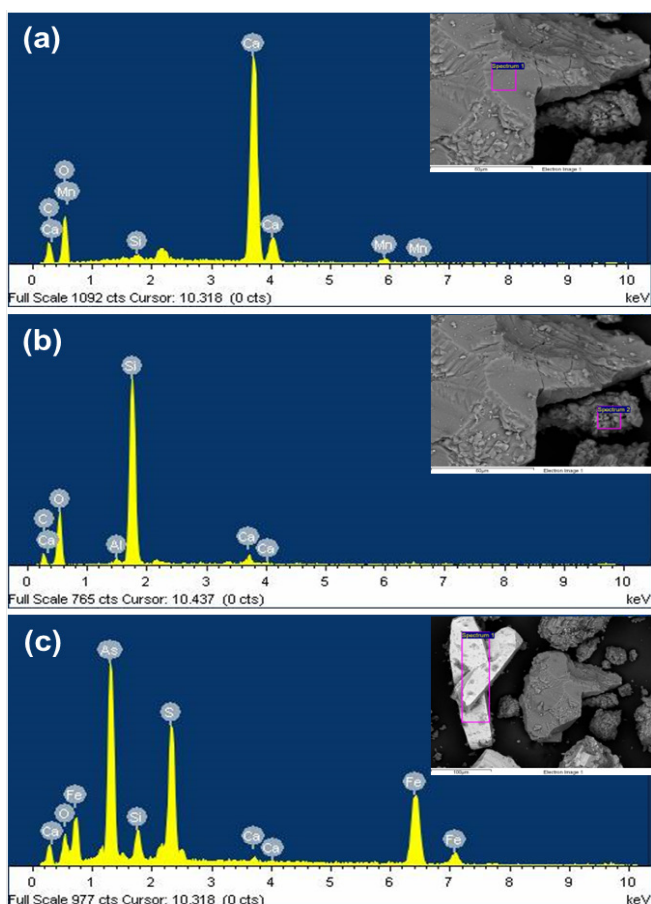

Figure 2. EDS spectra for different particles of sample CM-1 identified by SEM.

that the elemental composition of the particle corresponds to arsenopyrite, a mineralogical phase not detected by XRD. On the other hand, diffraction did not reveal any Mn-containing phase (Figure 2a), which is probably due to an amorphous component or an elemental substitution not identifiable by XRD.

Figure 3 shows the EDS spectra of two particles that, although appearing together, correspond to different minerals. In the case of Figure 3a, an elemental composition is observed which is consistent with the identification of silicates by XRD. In the case of Figure 3b, a composition mainly of sulfur and iron is observed, which can be associated with the pyrite content previously identified in the diffractogram. In general, the results of Figure 3 confirm the XRD identifications.
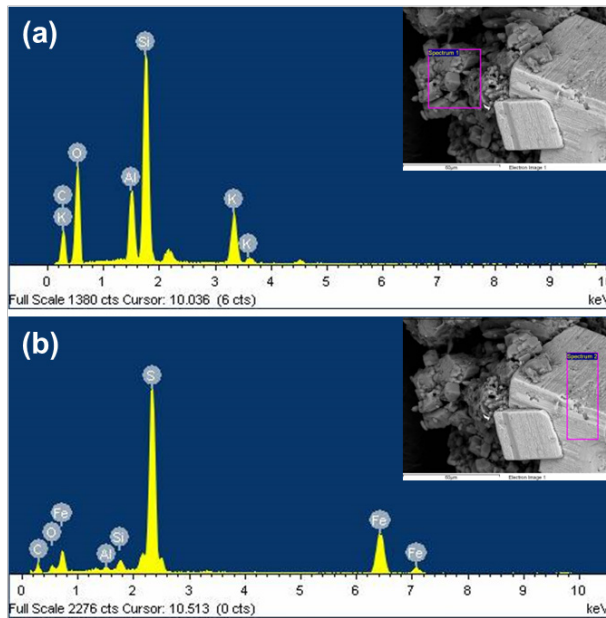

Figure 3. EDS spectra for different particles of sample CM-2 identified by SEM.

Figure 4 shows the EDS spectra of various particles from the sample SBC. In this case, more particles were analyzed because a greater variety was observed in the microscopic study. An elemental composition of the particles consistent mainly with silicates is observed. The calcium identified is associated with akermanite, margarite, and albite, unlike the previous samples, where this element was mainly associated with carbonates. Note that, in this sample, the presence of metallic sulfides is not identified by any method, but the presence of iron oxides can be inferred considering Figure 4e.
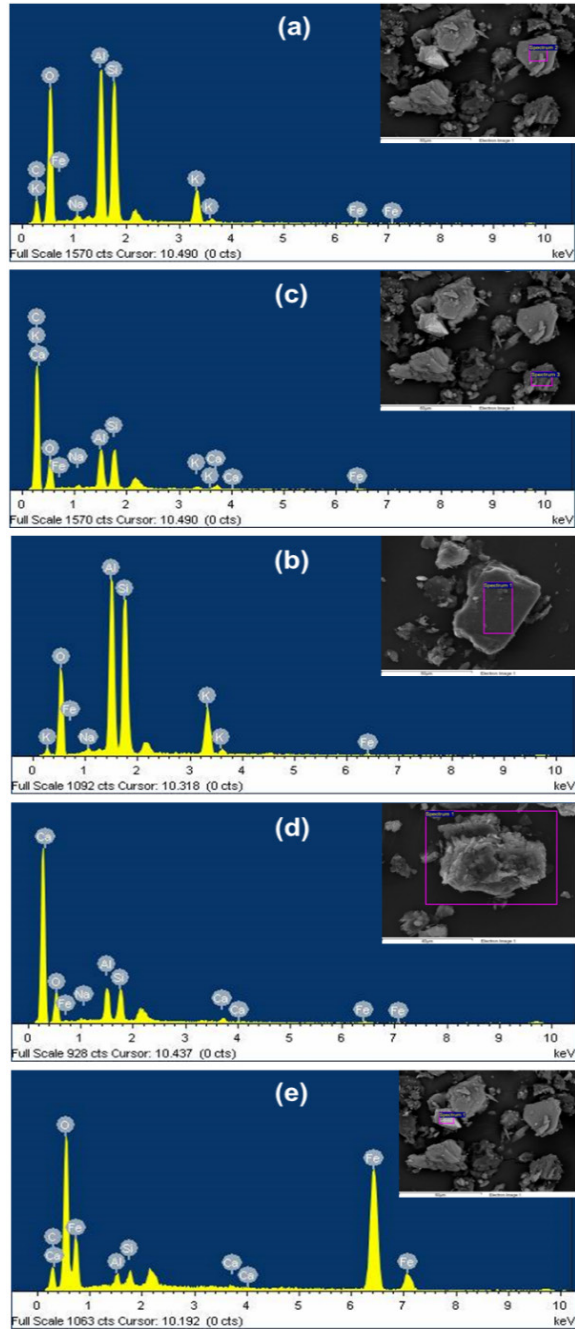
Figure 4. EDS spectra for different particles of sample SBC identified by SEM.

Quantification of carbonates, LOI, and TOC

Existing methods for TOC quantification generally have drawbacks. This has to do with the fact that ensuring the complete oxidation of organic matter is not as easy as it might be thought. The very marked differences that exist between different soil types and minerals, as well as the mineralogical associations in which organic matter is sometimes involved are aspects that influence TOC results. In addition, organic matter is very diverse, ranging from microbial biomass to high molecular weight organic compounds. All of this generally results in incomplete oxidation even under the most oxidizing conditions. Therefore, there is usually a proportionality factor between oxidized organic matter and TOC that can vary from one method to another [10]. However, these are empirical factors and although widely used, as in this work, they are not fully generalizable because oxidation is more complete in some samples than in others. On the other hand, interferences often produce very important effects in these analytical methods, such as the presence of chlorides, clays, or carbonates [9]. Nevertheless, these are the methods available, and some are more available than others depending on the laboratory. Therefore, the best solution to these problems is to establish procedures according to the type of sample.

Table 2 shows the results of the semi-quantification of inorganic carbon by XRD. It was only possible to determine the carbonate content in samples CM-1 and CM-2, corresponding to calcite in both cases and additionally to dolomite in CM-2, as previously observed in the diffractograms (Figure 1). In the case of sample SBC, the graphite content was determined.

Table 2. Semi-quantification of inorganic carbon by XRD
in mineral samples containing coal

Sample	Mineral phase	%
CM-1	Calcite	20.4
CM-2	Calcite, Dolomite	74.7, 0.7
SBC	Graphite	42.6

Table 3 shows the analytical results of the quantification of carbonates in the form of $CaCO_3$ for samples CM-1 and CM-2 using the Bernard calcimeter. Five quantifications were performed for each sample. It can be observed that, for sample CM-1, the content (18.6±0.9%) is much lower than for sample CM-2 (63.4±2.0%). These results are quite coincident with those obtained in the semi-quantification by XRD, which is an indicator that the analytical procedure is adequate.

Table 3. Quantification of carbonates in mineral samples containing coal using the Bernard calcimeter

	m (g)	V(CO_2, mL)	$CaCO_3$ (%)
CM-1	0.2002	6.1	18.7
	0.2007	6.5	19.9
	0.2010	6.1	18.7
	0.2005	5.7	17.5
	0.2011	5.9	18.0
Mean	**0.2007**	**6.1**	**18.6**
SD	**0.0004**	**0.3**	**0.9**
CM-2	0.2029	21.8	66.1
	0.2024	20.1	61.1
	0.2026	20.5	62.2
	0.2021	21.2	64.5
	0.2023	20.8	63.2
Mean	**0.2025**	**20.9**	**63.4**
SD	**0.0003**	**0.7**	**2.0**

$CaCO_3$ standard: m = 0.2002±0.0001 g, V(CO_2) = 32.55±0.21 mL

The gravimetric quantification of TOC is not new, however, the procedure and the temperatures at which the sample is treated vary greatly from one literature to another, and this is because it is highly dependent on the type of sample [9–11]. Table 4 shows the results of the quantification of carbonates, LOI, and TOC in samples CM-1 and CM-2 by the proposed gravimetric method. Each quantification was performed in triplicate. First, the carbonate content should be analyzed. For sample CM-1 it is 19.2±0.4%, while for sample CM-2 it is 70.3±2.4%. These values are similar to those obtained by XRD and Bernard calcimetry. However, a more rigorous criterion is the t-test for the comparison of the means obtained by gravimetry and calcimetry, shown in Table 5. The p-value for sample CM-1 is higher than the 0.05 significance level (95% confidence). This means that there are no statistically significant differences between the results obtained for this sample by the gravimetric method with acid treatment and the Bernard calcimetric method. However, this is not the case for sample CM-2, where the p-value is less than 0.05 and less than 0.01, which means that there are statistically significant differences at both the 95% and 99% confidence levels. This may be related to incomplete dissolution of carbonates during the acid treatment in the Bernard calcimeter, since the carbonate content in this sample is much higher than in sample CM-1. This can be inferred if it is considered that the result by gravimetry is higher than that obtained with the calcimeter. However, some acid dissolution effects of components other than carbonates, including organic matter, cannot be ruled out, which may also

overestimate the carbonate result by the gravimetric method. Note how the relative standard deviation (RSD) increases dramatically for the analysis of sample CM-2 compared to CM-1, especially for LOI and TOC. In addition to the acid dissolution mentioned above, incomplete dissolution of carbonates may also occur, leading overall to less homogeneous volatilization from one replicate to another during the combustion treatment at 1100°C. A more intensive treatment of the sample, i.e., using time longer than 2 h and a higher amount of acid may solve the problem of incomplete dissolution; even slightly increasing the temperature can help. However, if dissolution of other components occurs, its effect on the analytical result can be increased by applying more intensive conditions. In any case, it should be considered by the analyst as a possible source of error depending on the mineralogy of the sample and the carbonate content.

Table 4. Quantification of carbonates, LOI, and TOC by gravimetry in mineral samples containing coal

	$CaCO_3$ (%)	LOI (%)	TOC (%)
CM-1	19.1	3.3	1.9
	18.8	3.6	2.1
	19.6	3.7	2.1
Mean	**19.2**	**3.5**	**2.1**
SD	**0.4**	**0.2**	**0.1**
RSD (%)	**2.1**	**5.7**	**4.8**
CM-2	72.7	1.9	1.1
	70.1	2.5	1.4
	68.0	3.1	1.8
Mean	**70.3**	**2.5**	**1.4**
SD	**2.4**	**0.6**	**0.3**
RSD (%)	**3.4**	**24.0**	**21.4**

Table 5. T-test for the comparison between the carbonate results obtained by the Bernard calcimeter and the gravimetric method

Sample	t-statistic	p-value
CM-1	-1.07264	0.3247
CM-2	-4.4733	0.0042

In the case of TOC, it has been observed that the accuracy of the method can be lower depending on the type of sample, e.g., in sandy soils the RSD tends to be much higher than in forest floor samples when using the LOI method [12]. Furthermore, De Vos et al. [12] point out that the LOI-based

method is the most convenient but that its accuracy is questionable. In fact, Li et al. [11] show that the LOI method has the highest error and variability of results compared to wet oxidation with potassium dichromate and sulfuric acid. This allows to understand that the difference in precision for TOC observed in this work is common. Furthermore, this shows that the mineralogical and organic matter composition is the key to explain the variability of the LOI method. This is because the composition of the sample matrix defines the occurrence or not of interfering effects or incomplete volatilization effects. Nevertheless, the results obtained in this work are adequate for application in mineral and coal processing.

Figure 5 compares TOC determination for samples CM-1 and CM-2 with and without carbonate removal by acid treatment. This is to check the effect of incorrect processing of a carbonated sample. It is observed that when proper treatment is not performed on carbonates, the TOC results are incorrect, and the variability of the results is greatly increased. This supports the above discussion of how necessary the complete removal of carbonates in mineral samples is for accurate TOC quantification.
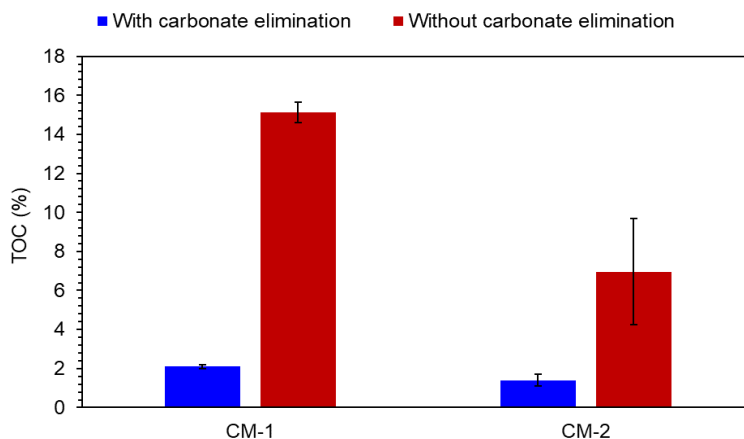

Figure 5. TOC values of samples CM-1 and CM-2 with and without carbonate elimination.

Figure 6 shows that, in samples with absence of carbonates, such as the sub-bituminous coal analyzed, it is not necessary to perform acid treatment with HCl, clearly observing how the result with and without treatment is practically the same. In fact, a t-test revealed a p-value greater than 0.05 (t-statistic = 1.4321, p-value = 0.2254), which allows affirming that there are no statistically significant differences for 95% confidence.

The conversion factor of 0.58 between TOC and organic matter was not applied to the LOI determined for the SBC sample because the content lost after ignition at 1100°C closely matches the percentage of graphite obtained by XRD (42.6%), indicating that the substance combusted was mainly graphite. Graphite normally ignites at temperatures below 800°C and combustion is complete before 1000°C [15–17], so it is to be expected that at 1100°C this material would be lost. A t-test showed that the LOI quantified without acid treatment (46.2±0.4%) is not statistically equal to the graphite content obtained by XRD for either 95% or 99% confidence (t-statistic = 14.5815, p-value = 0.0047). This indicates that probably, the 3.6% difference between both values corresponds to organic matter, whose TOC would be 2.1% (3.6×0.58). However, the XRD method is semi-quantitative, so this analysis is not analytically reliable. Since the graphite content is in the major part anyway (44.1%, 21 times higher than 2.1%), it is preferable in this case to assume LOI as a measure of carbon content other than carbonates. To be more rigorous, it is necessary to apply a refinement method for XRD to quantify the graphite phase. However, the application of carbon quantification in mineral and coal processing does not require these levels of analytical performance. Nevertheless, this demonstrates the importance of knowing the mineralogy of the sample before applying an analytical procedure to determine TOC and carbonates.
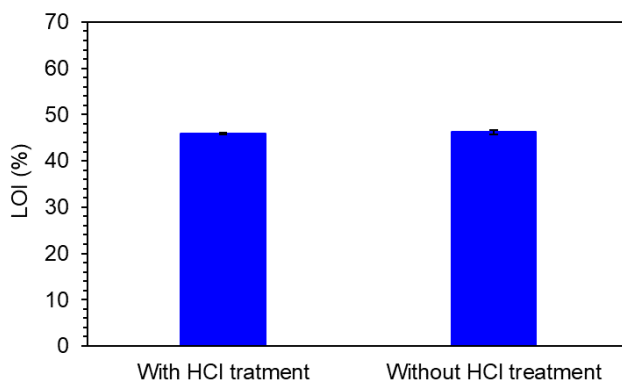

Figure 6. LOI values for the sample SBC without and with HCl treatment to remove carbonates.

Morphological study

Figure 7 shows the backscattered electron micrographs of the three samples before any treatment, after acid treatment, and after heat treatment at 1100°C. In the case of sample CM-1, Figure 7a shows particles with different

morphologies and brightnesses associated with different minerals released as
a result of the grinding process to which each sample was subjected. After the
acid treatment, no significant change in morphology is observed (Figure 7b), but
after the high temperature treatment, some fractured particles are observed
due to the heat effect (Figure 7c). The same behavior is observed for sample
CM-2 (Figures 7d-f). In an EDS analysis, these fractured particles were
identified as iron oxides. In the case of sample SBC, Figures 7g-i do not show
marked differences in brightness and morphology as in the case of the two
previous samples. This is because this sample has a less varied composition
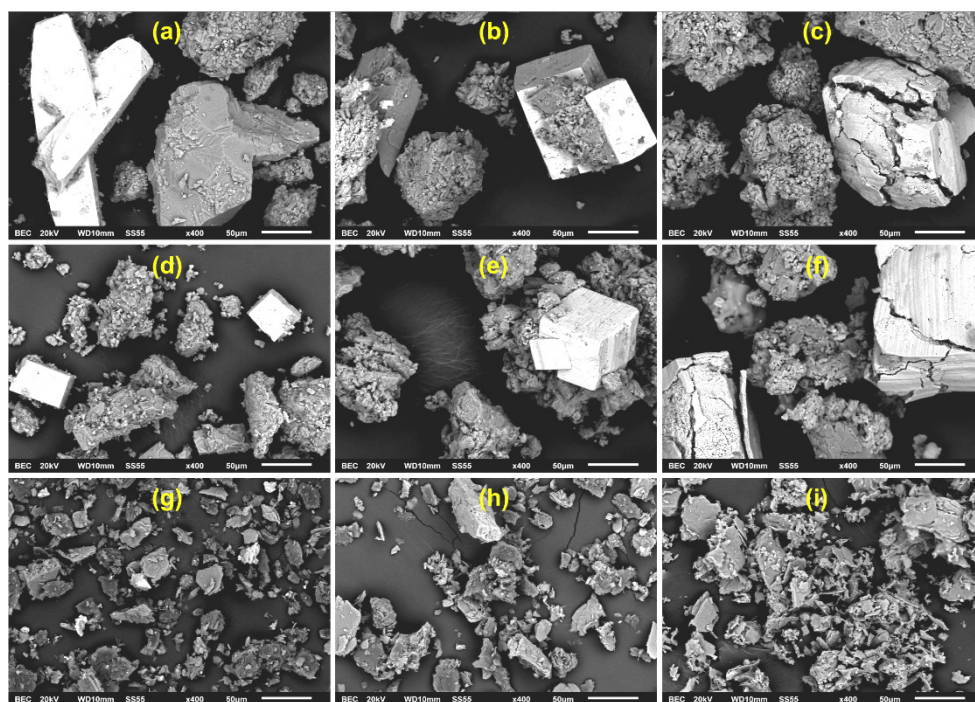in terms of mineral type (only silicates and graphite), as observed by XRD.

Figure 7. Scanning electron micrographs: (a-c) Sample CM-1 before any treatment,
after acid treatment, and after heat treatment at 1100°C, respectively. (d-f) Sample
CM-2 before any treatment, after acid treatment, and after heat treatment at 1100°C,
respectively. (g-i) Sample SBC before any treatment, after acid treatment, and after
heat treatment at 1100°C, respectively.

Conclusions

Quantification of TOC and carbonates is possible in the same gravimetric procedure for mineral samples containing coal. Carbonates play a fundamental role in the accuracy of the gravimetric loss-on-ignition method for TOC determination. They must be identified prior to analysis and, if found, must be removed by acid treatment, the extent and intensity of which will depend on the amount present. It is necessary to consider the incomplete dissolution of carbonates as well as the dissolution of other components as possible sources of error in the gravimetric method. Samples free of carbonates do not require acid treatment for TOC quantification. Knowing the mineralogy of the rock is essential to accurately analyze both the organic and inorganic carbon content in samples containing coal and other minerals.

EXPERIMENTAL SECTION

Mineralogical and morphological characterization of the samples

The mineralogical composition of the samples was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) analyzer. The XRD method was performed with a Bruker D8-Advance diffractometer operated at 30 kV using a wavelength of 1.5406 Å. For the electron microscopy, a JEOL JSM-6610LV scanning microscope operated at 20 kV was used. The morphology of the samples was studied using this microscope with a backscattered electron detector. For all samples, grinding and milling was performed to a particle size of less than 100 µm.

Identification and quantification of carbonates as CaCO3

Quantification of carbonates as $CaCO_3$ was performed using a Bernard calcimeter (Figure 8). This apparatus consists of a hermetically sealed vessel containing the sample and a small glass or stainless-steel vessel containing 50% HCl. This vessel or chamber is connected by a hose to the top of a column with a scale (it can be a burette) that allows the gas volume to be measured using a liquid column consisting of a CO_2 saturated solution stained with methyl orange. The saturated solution prevents some of the carbon dioxide from dissolving in the water. When the containing chamber is agitated enough to spill the HCl over the sample, a reaction occurs that releases CO_2. The gas displaces the colored liquid column, allowing a liquid

level equivalent to the gas volume to be measured. The displacement of the liquid column is related to the carbonate concentration using a substance as a standard, usually calcium carbonate [18,19].
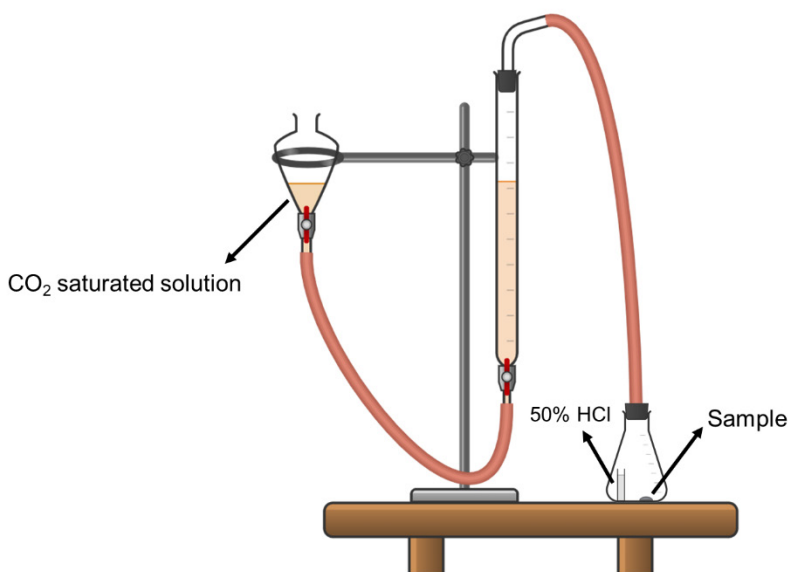

Figure 8. Schematic of the Bernard calcimeter used for the determination of carbonates in mineral samples containing coal.

Prior to the determination, a saturated CO_2 solution was prepared by mixing 350 mL of deionized water with 1 g $NaHCO_3$ and 100 g NaCl. Subsequently, a 1 mol/L H_2SO_4 solution was added until a slight acid reaction with CO_2 release was provoked. Then, a few drops of methyl orange were added to facilitate the visualization of the CO_2 volume on the measuring scale. For quantification with the calcimeter, 0.2 g of mineral was used, and as carbonate standard, 0.2 g of dry $CaCO_3$ (105°C for 2 h). Equation 1 was used to calculate the calcium carbonate content in the samples.

$$CaCO_3(\%) = \frac{V(CO_2)_{mineral} \times m\ (CaCO_3)}{V(CO_2)_{CaCO_3} \times m\ (mineral)} \times 100 \qquad (1)$$

Where V is the volume of liquid displaced (mL), m is the mass (g).

Gravimetric procedure for TOC and carbonate quantification in mineral samples with coal content

The procedure established for the determination of TOC and carbonates by gravimetry in the sample types used in this work is shown in Figure 9. First, the rock is ground and milled to a fine powder (< 100 μm). Before proceeding with the analytical determination, it is important to know whether carbonates are present, which can be done by XRD, acid test with concentrated HCl, or prior mineralogical identification by optical or electron microscopy. The qualitative acid test is based on the reaction of carbonates with hydrogen ions to release CO_2, which causes bubbling. However, it is important to note that this test may lack sensitivity when the amount of carbonates is very small. If there is any uncertainty about the absence of carbonates, it is preferable to perform the procedure as if carbonates were present.

For both carbonate and non-carbonate containing samples, the first analytical step is the removal of moisture. To do this, 1 g of sample is weighed into a porcelain capsule and heat treated at 105°C for 4 h, then allowed to cool to room temperature in a desiccator and the capsule is weighed. It is placed again for 1 h in the oven, and after cooling in the desiccator, it is weighed again. This is done as many times as necessary until constant weight.

If carbonates are present, after removing the moisture, the sample is treated with an excess of 4 mol/L HCl; CO_2 bubbling will be observed, whose intensity and duration depend on the amount of carbonates. When the bubbling stops, it is necessary to wait 2 h for the decomposition reaction to complete. The solution is then carefully removed with a Pasteur pipette. This step may be problematic if suspended solids remain after the 2 h rest period. In this case, it is advisable to centrifuge the mixture to avoid the loss of solids. It is important to note that it is not necessary to remove all of the solution, but to remove a sufficient amount until, due to the small amount of solution, there is a risk of extracting solids with the pipette. After removing as much of the solution as possible, the solid is dried at 70°C for 2 h. This step does not require complete drying of the solid, but it is necessary to evaporate all the liquid, so if 2 h is not sufficient, the treatment should be extended. After the treatment at 70°C, the chlorides remaining from the acid elimination of the carbonates are removed. This is done by washing the solid with a sufficient amount of water until no chloride is detected in the qualitative analysis with 1% silver nitrate, which gives a white solid as a positive result. When all chloride has been removed, the moisture in the sample is eliminated by heat treatment at 105°C for 24 h.
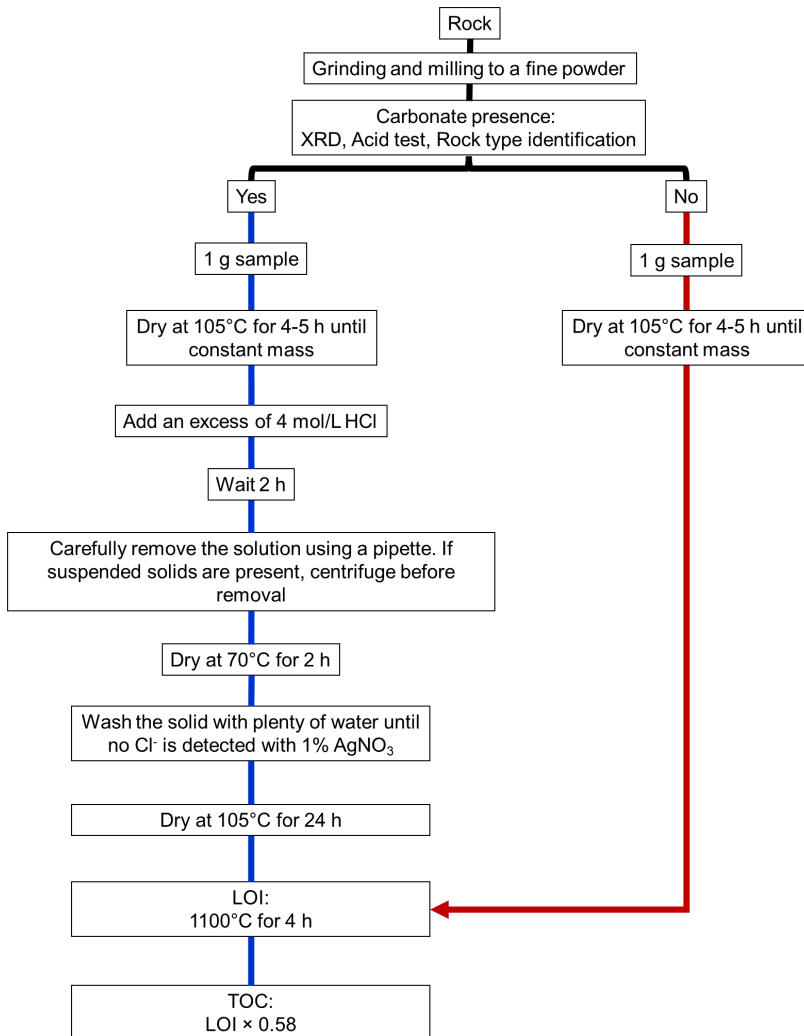
Figure 9. Step-by-step diagram of the analytical procedure for the gravimetric
determination of TOC and carbonates in mineral samples containing coal.

Subsequently, heat treatment is carried out at 1100°C for 4 h to ignite
the organic matter. This allows the LOI to be calculated as the difference in
mass before and after the calcination treatment. Equation 2 shows how to
calculate the TOC after the procedure. Dividing the LOI by the sample mass
and then multiplying by 100 allows the percentage LOI to be calculated,
which is related to the TOC by a factor of 0.58 (1/1.724) [11].

For a carbonate-free sample, 1 g of sample is weighed, and the moisture is removed as above. After this step, the LOI is determined gravimetrically as described previously.

$$TOC(\%) = \frac{m_{105°C(24h)} - m_{1100°C}}{m_{sample}} \times 100 \times 0.58 \qquad (2)$$

Where $m_{105°C(24h)}$ is the sample mass (g) after acid treatment and drying at 105°C for 24 h, $m_{1100°C}$ is the sample mass (g) after calcination at 1100°C for 4 h, m_{sample} is the sample mass (g) weighed initially.

The quantification of carbonates is implicit in the procedure shown in Figure 9. These are calculated as the difference between the sample mass before acid treatment with 4 mol/L HCl (after moisture removal) and the sample mass after acid treatment (after drying at 105°C for 24 h). The gravimetric calculation is performed according to Equation 3.

$$CaCO_3(\%) = \frac{m_{105°C(4h)} - m_{105°C(24h)}}{m_{sample}} \times 100 \qquad (3)$$

Where $m_{105°C(4h)}$ is the sample mass (g) after removal of moisture at 105°C for at least 4 h, $m_{105°C(24h)}$ is the sample mass (g) after acid treatment and drying at 105°C for 24 h, m_{sample} is the sample mass (g) weighed initially.

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