DETERMINATION OF ORGANIC CARBON IN CERAMIC RAW MATERIALS, IN THE PRESENCE OF SIDERITE, TO CONTROL BLACK CORING

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1. INTRODUCTION

In ceramic tile manufacture, clays are used that customarily contain organic matter as an impurity. During the firing process a so-called 'black core' can appear inside the tile, which is related to the organic carbon concentration (C_{org}) in the compositions used to prepare the tile bodies. The appearance of black coring is favoured by the use of short firing cycles, the manufacture of large tile sizes in which compaction is increased, leading to a lower diffusion coefficient, etc. Black coring is considered a defect because it can give rise to lower mechanical strength in vitreous materials, tile bloating, pyroplastic deformation, alterations in the body and/or glaze colour, etc. C_{org} is therefore a key variable to be considered in the raw materials used in the manufacture of ceramic tile bodies.

Ceramic raw materials generally contain C_{org} at a $mg \cdot kg^{-1}$ level, in addition to inorganic carbon (C_{inorg}) at a percentage level, C_{inorg} being mainly present in siderite ($FeCO_3$), calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$). However, the presence of siderite can interfere significantly in the determination of C_{org}, since its decomposition temperature differs very little from the temperature to which the material must be subjected to analyse C_{org}; this is not the case with calcite and dolomite, which have higher decomposition temperatures.

In this study, a method of determining C_{org} in raw materials and ceramic bodies in the presence of siderite was developed, in order to control black coring in ceramic tiles. The following variables were studied: type of elemental analyser, working temperature, interferences produced by the presence of $FeCO_3$, and relationship between organic carbon concentration and the appearance of black coring.

2. EXPERIMENTAL PART

The study was conducted with a series of clays and ceramic bodies used in floor and wall tile manufacture, in addition to the following reference materials: NCS DC 14038 Siderite, GBW 07401, GBW 07402, GBW 07403, GBW 07406, and GBW 07407.

The instruments used for the carbon determination were the LECO model RC-412, CS-200, and TruSpec CHNS elemental analysers.

The *RC-412 carbon elemental analyser* has an electric furnace that allows different types of carbon to be determined in samples, as it is equipped with a programmer that enables temperature ramps to be made. A schematic illustration of this instrument is shown in Figure 1.

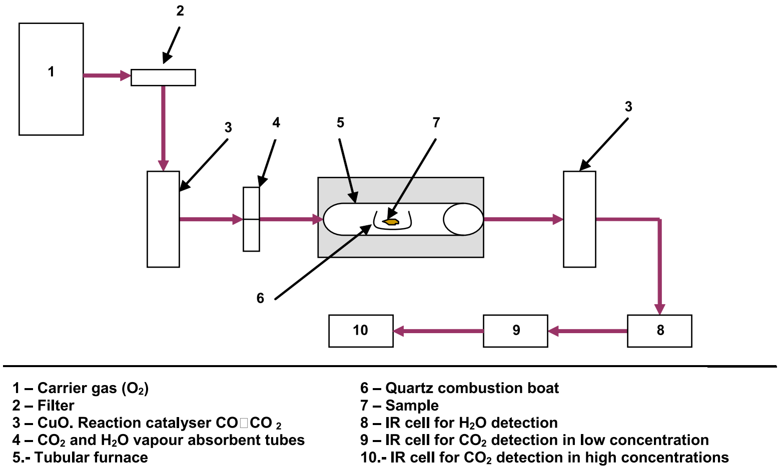


Figure 1. Scheme of the LECO RS-412 elemental analyser

The *CS-200 carbon elemental analyser* has an induction furnace that reaches very high temperatures (about 2000ºC), which allows total carbon in the sample to be determined. A schematic illustration of this instrument is shown in Figure 2.

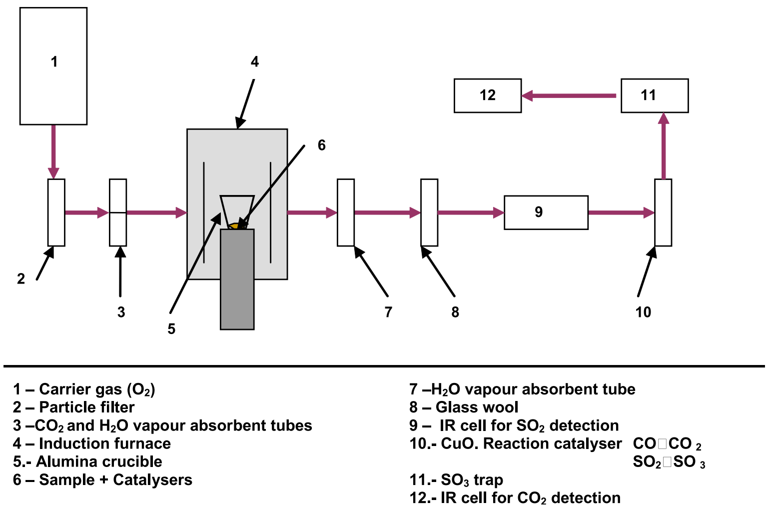
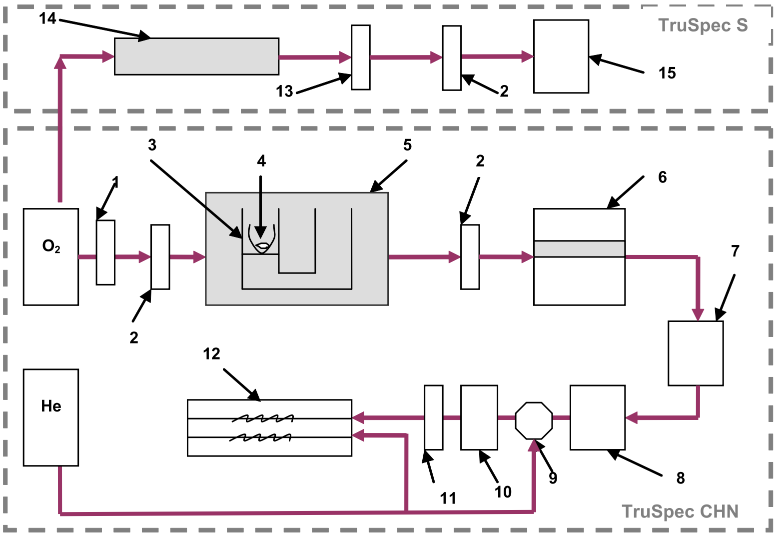


Figure 2. Scheme of the LECO CS-200 elemental analyser

The *TruSpec CHNS elemental analyser* has a programmable furnace for work at variable temperatures and, therefore, just as the RC-412 analyser, it enables both C_{org} and C_{inorg} to be determined. A schematic illustration of this instrument is shown in Figure 3.



1 – CO_2 and H_2O vapour absorbent tube
2 – Particle filters
3 – Crucible
4 – Sample
5 – Quartz furnace
6 – Homogenization vessel
7 –IR cell for H_2O detection
8 –IR cell for CO_2 detection
9 – Aliquot valve
10 – Cu + N. Catalyser for the elimination of O_2
Reaction catalyser NOx □ N_2
11 – CO_2 and H_2O vapour absorbent tube
12 – N_2 Thermal conductivity detector
13 –H_2O vapour absorbent tube
14 – Tubular furnace
15 – SO_2 detector

Figure 3. Scheme of the LECO TruSpec CHNS elemental analyser

To identify the most appropriate instrument for determining C_{org}, the reference materials were analysed with the RC-412 and TruSpec CHNS analysers.

To establish the optimum temperature, three temperatures were tested: 490ºC, 500ºC, and 540ºC, and the reference materials, clays, and mixtures of clays with siderite were analysed. The temperature was thus determined at which 100% analyte recovery and minimum interference were obtained.

In order to be able to analyse C_{org} when the instrument is unable to work at variable temperatures (electric furnace), but has an induction furnace, it is necessary to pre-treat the sample, with a view to eliminating any interferences that the C_{inorg}, stemming from siderite, calcite, dolomite, etc., might cause in the C_{org} measurement. This was done by subjecting the test samples to treatment with HCl solution under different conditions and then determining carbon in the induction furnace.

To study the relationship between C_{org} and black core formation in the firing process, C_{org} was determined in three clays and three spray-dried powders, and the tendency to form a black core was studied.

3. RESULTS

3.1. Most appropriate studied instrument for the determination of C_{org}

Table 1 details the results obtained in the determination of C_{org} in the reference materials using the RC-412 and TruSpec elemental analysers at a temperature of 500ºC. The results obtained were compared with the values recommended by the Sutarno-Steger test, calculating the parameter z, so that if z<2, the method is traceable.

Reference material	Known value (% C_{org})	RC-412 (500ºC)				TruSpec (500ºC)			
		$X_{obtained}$ (% C_{org})	u (%)	n	z	$X_{obtained}$ (% C_{org})	u (%)	n	z
GBW 07401	1.80±0.16	1.81	0.03	10	0.06	1.82	0.02	10	0.13
GBW 07402	0.49 ± 0.07	0.51	0.02	27	0.29	0.49	0.01	10	0.00
GBW 07403	0.51 ± 0.03	0.52	0.02	10	0.33	0.51	0.01	10	0.00
GBW 07406	0.81±0.09	0.80	0.03	10	0.11	0.83	0.01	10	0.22
GBW 07407	0.64±0.07	0.65	0.03	10	0.14	0.67	0.01	10	0.43

Table 1: Results of the determination of C_{org} in a series of soil reference materials using the RC-412 and TruSpec analysers

The results show that values of z<2 were obtained for all analysed materials by both instruments, so that the values obtained were acceptable. However, lower uncertainties were found in the measurements with the TruSpec analyser, which made this the better of the two instruments.

3.2. Optimisation of the working temperature

The optimum working temperature obtained was 490ºC: at this temperature, no appreciable differences were observed in the results in comparison with those obtained in the tests performed at 500ºC and 540ºC, while any possible decomposition of siderite was avoided.

3.3. Effect of the presence of siderite on the determination of C_{org}

Table 2 presents the results obtained in the determination of C_{org} in three clay samples to which a certain concentration of siderite was added. It also details the results of the carbon determination of the samples, before and after treatment with 50% HCl solution.

Sample	% C_{org} (490ºC) (Electric furnace)		% C total (Induction furnace)		
	Known value	Value obtained	Known value	Treated with HCl	Value obtained
CLAY 1	0.35	0.35	2.15	No	2.18
CLAY 1 + 5% NCS Siderite	0.35	0.34	2.67	No	2.63
				Yes	0.36
CLAY 2	0.08	0.09	1.72	No	1.75
CLAY 2 + 5% NCS Siderite	0.08	0.08	2.24	No	2.26
				Yes	0.09
CLAY 3	0.12	0.11	0.92	No	0.90
CLAY 3 + 5% NCS Siderite	0.12	0.12	1.44	No	1.45
				Yes	0.12

Table 2: Results of the study of the effect of siderite concentration on the C_{org} determination

The results show that there were no significant differences between the values of C_{org} of the samples without and with a siderite addition, which confirms that at this temperature, with the instrument used, the siderite did not interfere in the C_{org} analysis. In addition, the treatment with HCl effectively eliminated the carbonates in the analysed samples, since the resulting carbon values matched the C_{org} values in the samples treated with HCl. It may, therefore, be inferred that organic carbon can be determined in an instrument with an induction furnace if the sample is previously treated with 50% HCl solution to eliminate carbonates, though the detection limit would be higher than that of an instrument that was able to work at a programmable temperature of 490ºC.

3.4. Relationship between the concentration of C_{org} and black coring

The results of the determination of C_{org} in clays and spray-dried powders, as well as the tendency to form a black core, are detailed in Table 3 and Figure 4.

Sample	% C organic (490ºC)
Clay A	0.32
Clay B	0.15
Clay C	0.03
Spray-dried powder A	0.01
Spray-dried powder B	0.05
Spray-dried powder C	0.08

Table 3: Results obtained in the determination of C_{org} in clays and spray-dried powders

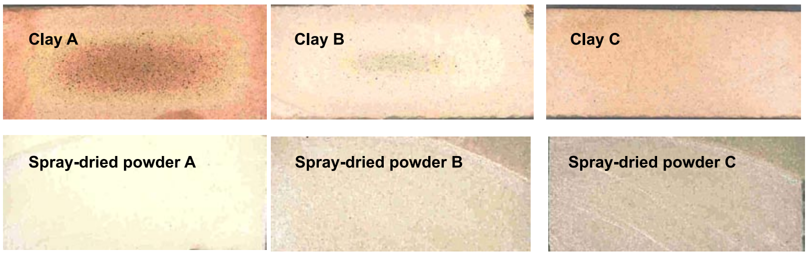


Figure 4. Tendency to black coring in clays A, B, and C and spray-dried powders A, B, and C

The results obtained show that the samples in which black core formation was clearly evidenced were clays A and B, which displayed a greater concentration of C_{org}. In addition, there was a good correlation between the values of C_{org} and the tendency to black core formation under the test conditions used, though the presence of black coring was only observed for values of C_{org} above 0.08%. The method of determining C_{org} was therefore more sensitive to the presence of organic matter than the black core formation test, though this test reproduces industrial conditions and consequently provides valuable information on the problem that the organic matter in a material can generate, since the processing conditions of the material significantly influence black core formation.

4. CONCLUSIONS

The study allows the following conclusions to be drawn:

1. The best tested instrument for carrying out C_{org} analysis without requiring sample pre-treatment was the TruSpec CHNS elemental analyser.
2. The appropriate decomposition temperature for determining C_{org}, without any siderite interference being observed in the samples, was 490ºC.
3. C_{org} can be determined with an instrument that has an induction furnace if the sample is previously treated with HCl and the carbonates that it contains are completely eliminated.
4. There is a correlation between the organic carbon concentration and the appearance of black core. It was observed that the method of determining C_{org} was more sensitive to the presence of organic matter than the black core formation test. However, determining only the value of C_{org} would not be sufficient to predict the behaviour of the material, since the processing conditions of the material significantly influence the tendency to black coring.

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