



## Determination of organic oxygen in petroleum cokes and coals



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### ABSTRACT

The accuracy of the oxygen value is important in calculating heat balances for boiler efficiency studies in coke and coal industry, and these data are used for determining the suitability of coals for coking, liquefaction, or gasification processes. Nowadays, organic oxygen is normally estimated by subtracting the determined percentages of all other constituents (carbon, hydrogen, nitrogen, sulphur, and ash content) from 100, so the errors in the determined values are reflected in the estimated organic oxygen value.

This paper describes a rapid and reliable methodology for the analysis of organic oxygen in petroleum cokes and coals using a pyrolysis furnace followed by IR detection, calculating the detection and quantification limits and the uncertainty of the method. The accuracy of the method has been also checked by analyzing reference materials and determining all the constituents (C, H, N, S, and ash content) of the petroleum cokes and coals analysed in this study. The organic oxygen data have been also correlated with the volatile matter as the oxygen-containing compounds constitute part of the total volatile matter and this parameter is important in the selection of coals and in the evaluation of coking of coke which will determine the use of the coke.

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### 1. Introduction

The chemical characterization of coals and cokes is normally divided into three categories: proximate analysis, ultimate analysis, and miscellaneous analysis. Proximate analysis is the determination, by prescribed methods, of the contents of moisture, volatile matter, ash, and fixed carbon. Ultimate analysis involves the determination of carbon and hydrogen content as found in the gaseous products of the complete combustion of the petroleum coke or coal, the determination of total sulphur, nitrogen, and ash content in the material as a whole, and the estimation of oxygen content by difference. Miscellaneous analysis is a collective category for various types of physical and chemical tests that are commonly requested by producers and buyers.

Oxygen is the most abundant heteroatom in coal; nevertheless, the direct quantification of the organic oxygen species remains a formidable analytical challenge [1]. Oxygen data are used for determining the suitability of coals for coking, liquefaction, or gasification processes. In general, coals with high oxygen content are unsuitable for coking but may be more reactive and thus easier to gasify or liquefy [2]. For coking coals, the organic oxygen may indicate undesirable weathering that will have a negative impact on coke quality [3].

The content of organic oxygen in coals and cokes is normally obtained by calculation as the difference of the sum of carbon, hydrogen, nitrogen, sulphur, and ashes from 100, thus presenting a huge uncertainty, coming

from the sum of all the uncertainties of all the components present in the sample. This estimated value is affected by errors incurred in the determinations of the values for the other elements and by changes in the weight of the ash-forming constituents on ignition. So, the development of a reliable and rapid method capable of determining the oxygen content in coals and cokes is of special interest.

Different studies related to the analysis of oxygen in organic compounds can be found [4–9]. About the analysis in organic materials, Kuck reported that he was able to obtain satisfactory results on compounds such as acetanilide but not on compounds such as benzoic acid, attributing this to not having a sufficient length of carbon filling at 1120 °C to effect complete reduction of the carbon dioxide formed by decarboxylation of the benzoic acid [10] and in other studies the analysis of oxygen in organic compounds has been carried out by titration [11] and by neutron activation [12,13]. About the analysis of the organic oxygen in coals, different papers have been found where different techniques of quantification have been used. The determination of the total organic oxygen has been carried out by thermogravimetry Fourier transform infrared spectroscopy (TG-FTIR), fast neutron activation analysis (FNAA), or pyrolysis–gas chromatography by different authors [3,14–18]. Others use techniques such as the acetylation–hydrolysis and ion-exchange and titration methods, and solid-state C NMR measurement [19], or XPS [1] to analyse the distribution of oxygen–functional groups in coals. The main oxygen–functional groups found in coals have been mainly carboxyl, carbonyl, and hydroxyl. All these techniques are quite tedious and the oxygen determination is still being carried out by difference.

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However, in a previous study [20], the necessity to analyse oxygen in petroleum products instead of calculating it by difference between 100% and the sum of all the other elements is already pointed out. It enumerates the interferences generated by the presence of sulphur, nitrogen, and halogens in the process of pyrolysis. Moreover, it is also brought out that the value obtained for the ash content is not a true indicator of the non-combustible material occurring in a petroleum coke or coal. The indefinite amounts of sulphur that may be retained in the ash make it difficult to give an exact interpretation of the ash content. The determination of ultimate analysis of coal and petroleum coke is defined in ASTM 3176 as the determination of carbon, hydrogen, sulphur, nitrogen, oxygen, and ash content. In this standard, oxygen is calculated by subtracting the sum of the percentages of C, H, N, S, and ash from 100, as there is no direct standard method of determining oxygen content [2, 21]. Others have studied how to solve the interference of sulphur by adding copper in the analysis process of oxygen [22,23]. Finally, a set of papers about the analysis of eight coals under the Argonne premium coal sample program were found [24,25], which intention was to provide the coal research community with the best-quality samples for basic research, carrying out the proximate analysis (moisture, ash, volatile matter, and fixed carbon), the ultimate analysis (C, H, S, N, O), the major and minor elements in the ash, and the equilibrium moisture. Although this set of materials was studied to benefit the coal research community, different data about organic oxygen, expressed in different bases, have been found depending on the paper consulted. Table 1 summarises some of diverse oxygen data found in the literature.

The data shown are just an example of the disparity of results that can be found and the various ways of expressing the data could lead to errors. To conduct the study shown in this paper, results obtained will be compared with the analytical data obtained from the Argonne National Laboratory Premium Coal Sample (data obtained from reference [26] in Table 1) as it is the primary data.

As the organic oxygen groups present in coals are volatile, it is expected that the oxygen content is correlated with volatile matter [29]. The volatile matter of coals is composed of materials that form upon the thermal decomposition of the various components of coals. Some of the constituents are hydrogen carbon monoxide, methane, and other hydrocarbons, tar vapours, ammonia, some organic sulphur and oxygen-containing compounds, and incombustible gases, such as carbon dioxide and water vapour, all of which come from the decomposition of organic materials in coals. This parameter is important in the selection of coals and in determining the blending proportions of coal for coking. In a coke, this value is used as a means of evaluating the extent of coking, depending on the intended use of the coke. It is also valuable to combustion engineers in setting up and maintaining proper burning rates [2].

The main objective of this paper is the development of a rapid and reliable method that allows the determination of oxygen in petroleum cokes and coals using a pyrolysis furnace followed by IR detection, as well as correlation of the values of organic oxygen obtained with those of volatile matter.

## 2. Experimental

In order to develop the method, an initial exhaustive search of reference materials that could be used in the calibration and validation processes was undertaken.

### 2.1. Materials

#### 2.1.1. Reference materials and coke materials coming from round robin tests with a known oxygen content

There are not many reference materials with the oxygen content analysed. Table 2 shows a list of reference materials available in our laboratory, used to carry out the study.

#### 2.1.2. Other reference materials of petroleum coke and coal and coke materials coming from round robin tests

Apart from the reference materials listed in Table 2, the laboratory has other reference materials of petroleum coke and coal as well as petroleum cokes coming from a round robin test which oxygen concentration is unknown but with the C, H, N, S, and ash content known, which are listed in Table 3.

### 2.2. Equipment

#### 2.2.1. Instrument

The determination of organic oxygen was carried out with a LECO model TruSpec CHNSO. The instrument is composed of three modules: the C, H, and N module; the S module, and the O module. The oxygen module consists of a pyrolysis furnace working at a temperature of 1300 °C. In turn, the furnace is composed by an outer ceramic reaction tube and an inner glassy carbon reaction tube. The sample is weighed into a tin capsule and dropped into a graphite crucible placed inside the glassy carbon reaction tube, lying on a carbon black bed. The sample is cracked and the oxygen released during the pyrolysis of the sample reacts with the carbon-rich environment inside the furnace to form CO. The CO and the rest of gaseous reaction products are swept from the furnace and a helium stream is used as a carrier. The CO stream is converted to CO<sub>2</sub> in a copper oxide catalyser before being measured via infrared detector. The infrared cell used for the measurement is placed in the C, H, and N module, measuring CO<sub>2</sub> which is later convert to oxygen percentage.

The instrument configuration makes it necessary to weigh between 1 and 3 mg of sample as it has to be weighed in a small tin capsule of reduced dimensions. The amount of sample weighed will depend on the expected oxygen content in the sample, just to avoid the saturation of the detection system.

#### 2.2.2. Carrier gas

The gas used as a carrier is helium with a purity of at least 99.9992%.

**Table 1**

Data of organic oxygen of the Argonne premium coals found in the literature.

References	(wt%) (dry basis)					(wt%) (daf) <sup>a</sup>		(wt%) (dmmf) <sup>b</sup>	(O per 100 carbons)		
	[3]	[3]	[17]	[17]	[26]	[27,28]	[27,28]	[27,28]	[1]	[1]	[1]
APCS-1	4.83	4.84	2.90	3.98	6.5	8	7.51	4.72	4.5	4.0	2.5
APCS-2	17.73	17.13	14.31	15.21	16.4	18	18.02	16.90	16.9	16.7	14.1
APCS-3	8.48	8.65	7.41	8.21	11.4	14	13.51	10.11	10.9	9.4	6.9
APCS-4	6.25	6.74	6.74	6.13	8.0	9	8.83	6.90	8.0	6.1	6.0
APCS-5	2.67	2.36	1.59	1.57	2.4	2	2.47	1.66	3.2	1.4	1.3
APCS-6	9.47	10.79	9.76	10.29	11.1	12	11.58	10.88	10.0	10.0	9.0
APCS-7	6.92	7.79	5.75	5.17	7.9	10	9.83	6.68	7.8	16.7	5.0
APCS-8	20.56	19.29	17.21	17.01	18.3	20	20.34	19.13	18.8	19.4	17.4

<sup>a</sup> daf = dry ash free basis.

<sup>b</sup> dmmf = dry mineral matter free basis.

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