Carbonization and demineralization of coals: A study by means of FT–IR spectroscopy

V GÓMEZ-SERRANO, M C FERNÁNDEZ-GONZÁLEZ, M L ROJAS-CERVANTES[†], M F ALEXANDRE-FRANCO and A MACÍAS-GARCÍA*

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Extremadura, 06071 Badajoz, Spain
*Área de Ciencia de Materiales e Ingeniería Metalúrgica, Escuela de Ingenierías Industriales, Universidad de Extremadura, 06071 Badajoz, Spain
[†]Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, 28040 Madrid, Spain

Abstract. Coal basically consists of two parts—a crystalline, inorganic part, and an amorphous, organic part. Based on this, we intended to study the changes that occurred on the composition and on the chemical structure of coals after carbonization at 1000 or 900°C and demineralization treatments with hydrochloric and hydrofluoric acids. For this, four coals of different categories (or levels) were chosen: semianthracite (A–O) and high volatile bituminous coal (B–O), which are high level coals, and lignite (Li–O) and leonardite (Le–O), these being low level coals. The coals were first analysed in terms of their proximate and elemental compositions and then carbonized and demineralized. Also, the starting coals and the prepared samples were examined by infrared spectroscopy. In addition, a study of the optimization of the application of this technique for only A–O was carried out. For A–O and B–O, the spectra recorded intense absorption bands that are ascribable to vibration modes in mineral components as quartz and aluminosilicates, such as kaolinite. For Li–O and Le–O, the spectra displayed some other bands as well, also quite intense, which have been assigned to bond vibrations in functional groups and structures of their organic part. The carbonization of the coals resulted in significant changes in their inorganic part as the content of quartz increased and the content of aluminosilicates decreased. In addition, the thermal decomposition of mineral carbonates occurred. The carbonization greatly affects the organic part of the coals, especially in Li–O and Le–O, as most functional groups and structures are not thermally stable under heating conditions. With regard to demineralization, HF is a more effective agent than HCl, achieving products with higher organic content. The mass losses are higher in Li–O and Le–O than in A–O and B–O. So, the infrared spectroscopy allows the analysis of both inorganic and organic parts of the coals and of their carbonization and demineralization products. These processes facilitate subsequent analysis of the inorganic and organic parts of coals by infrared spectroscopy. In the application of this technique, both the coal : KBr ratio and the thickness for the disks should be controlled, owing to the influence on the infrared absorption.

Keywords. Coals; carbonization; demineralization; infrared spectroscopy.

1. Introduction

Nowadays, coal is a mineral resource of great importance (Grainger and Gibson 1981). It basically consists of two parts—a crystalline, inorganic part, and an amorphous, organic part. Chemically, it is a complex mixture of organic compounds and mineral matter (impurities) containing around 30–40 different elements, mainly non-metals such as nitrogen, sulphur, phosphorus, and chlorine, and metals such as aluminium, calcium, iron, magnesium, potassium, etc (Given 1976). These impurities, when burned, form non-combustible residues known as ashes, of which silica is a very important component.

Coal being so heterogeneous and, thus, complex, it is rather difficult to characterize and know exactly its molecular structure. Hence, to date, none of the many proposed models (Spackman 1958; Given 1960, 1976; Spence and Vharman 1970; Vharman 1970; Wiser 1973; Larsen and Kovac 1978; Solomon 1981; van Krevelen 1981; Gavalas 1982; Marzec 1986; Hüttinger and Mchenfelder 1987; Lucht and Pepas 1987; Solomon *et al* 1988; Rouzaud 1990; Carlson 1991; Carlson and Grannoff 1991; Muntean and Stock 1991; van Heek *et al* 1994; Kovac and Larsen 1997) has been accepted by the overall scientific community. The molecular structure of coal has been studied critically in several articles (Davidson 1982; Green *et al* 1982; Given 1984; Berkwitz 1987; Gorbaty 1994). Coal seems to consist of a three-dimensional network of chains formed by aromatic and hydro-aromatic

*Author for correspondence

units. Chains join themselves by covalent bonds, hydrogen bonds or Van der Waals forces (Spence and Vharman 1970; Vharman 1970; van Krevelen 1981; Lucht and Pepas 1987). Inside the three-dimensional network there are some lower-weighted molecular fragments, lightly bonded to or physically trapped into the pore system (macro-, meso- and micropores) of coal. Some of the occluded components in coal are extracted by appropriate solvents.

The chemical properties of a given coal depend mainly on the surface, porous texture and specific surface, on the minerals present in it, and on the functional groups that make up its primary structure. The functional groups vary according to the degree of metamorphism of the coal, i.e. its category or level, the most important ones being hydroxyl, carboxyl and carbonyl (Retcofsky 1975; Given 1976). A wide diversity of minerals have been found in coal (Speight 1990). They include clay minerals (hydrated aluminosilicates), silica (quartz), carbonates, sulphides, and so on. Of them, clay minerals are the most predominant minerals.

The main aim of this work was to investigate the changes that took place in the composition and chemical structure of coal after carbonization and demineralization. The analysis tool used in the study was FT–IR spectroscopy. As a secondary objective, the optimization of the application of FT–IR spectroscopy to the study of coal was also investigated.

2. Materials and experimental

Four coals were chosen for this study. Two were high level coals—semianthracite and high volatile bituminous coal—and the other two were low level coals—lignite and leonardite. Because of the different degrees of humidity present in the starting materials, the coals were oven-dried at 110°C until constant weight. Once cooled to room temperature in a dryer containing concentrated H_2SO_4 or $CaCl_2$, they were sieved to make a granulometric analysis. The fraction of particle sizes chosen was 0·15–0·20 mm for anthracite and high volatile bituminous coal and 0·10–0·40 mm for lignite and leonardite. Afterwards, the coals were chemically analysed by effecting the immediate and elemental analyses.

Coal samples were carbonized at 1000°C (anthracite and high volatile bituminous coal) and 900°C (lignite and leonardite) in N_2 (flow rate = 100 ml min^{-1}). Heating rate was 5°C min^{-1}. Isothermal time at maximum heat treatment temperature was 2 h. After that, the system was cooled down to room temperature in the same N_2 flow.

The methods of coal demineralization were based on physical and chemical processes. In this work, HCl and HF solutions were used with such an aim. Although the use of HF for the demineralization of coal may not be of industrial value, at a small laboratory scale the action of this acid is frequently investigated as it is dealt with a very effective

agent. In the treatments with HCl, 10 ml of HCl 5N was added per gram of coal to a 500 ml flask fitted with a refrigerant column and the mixture was boiled with reflux for 30 min. Once cooled, the solid residue was separated by filtration in a milled glass filter and washed first with HCl 5% and then thoroughly with distilled water till the silver nitrate test was negative. Subsequently, the samples were oven-dried at 110°C and stored in a dryer containing concentrated H_2SO_4.

After treatment with HCl, 4 ml of HF 48% was added per gram of resultant product to a plastic container, which was placed in a water bath. Then, the reaction mixture was heated at 85–90°C until dryness. Finally, using a china filter, the fluorides kept in the residual solid were washed-out with distilled water. The absence of fluoride was checked through the alizarin-S and zirconium test based in the formation of a red complex in absence of fluoride ions.

All samples (original, carbonized and demineralized products) were analysed by infrared spectroscopy, using KBr as dispersing and agglutinating agent to prepare disks before recording the spectra. Most disks were prepared in the proportion coal : KBr = 1 : 400, the total mass being 150 mg. The resulting mixture was placed in a Perkin-Elmer hydraulic press, and a charge of 10 tons was applied for 3 min. Only for a coal (i.e. A–O), disks were also prepared by varying the proportion of coal : KBr and their total mass, or thickness.

Spectra were recorded on a Perkin-Elmer 1720 spectrophotometer in the range of wave numbers 4000–450 cm^{-1}. 50 scans were made at 2 cm^{-1} resolution, which took 6·8 min. A background and reference spectrum registered previously for a KBr disk was subtracted from the spectrum of each sample. The mass and thickness of such a disk was identical to that for the sample. To better compare the results, all spectra were represented between 4000 and 450 cm^{-1}. Also, occasionally, the same scale was used in the transmission/absorption axis. Spectra were processed with the aid of a compatible PC. Samples were named as listed in table 1.

3. Results and discussion

3.1 *Chemical analyses of coals*

Data of the proximate analysis for the four starting coals are shown in table 2. As expected in view of the category

Table 1. Nomenclature of the samples.

Sample	Starting	Carbonized	Demineralized
Anthracite	A–O	A–C	A–D
High volatile bituminous coal	B–O	B–C	B–D
Lignite	Li–O	Li–C	Li–D
Leonardite	Le–O	Le–C	Le–D

Table 2. Chemical analyses of the starting coals (wt%).

Sample	Moisture	Volatile matter	Ashes	Fixed carbon*	C	H	N	S	O_{diff}**
A–O	1·9	8·5	38·7	50·9	49·2	2·1	1·0	0·6	7·7
B–O	2·3	18·5	49·6	29·6	38·7	2·5	0·8	0·6	6·7
Li–O	3·3	29·9	41·9	24·9	34·4	2·9	0·4	5·7	13·3
Le–O	4·4	34·9	34·6	26·1	38·4	3·0	0·6	1·7	20·1

*By difference; **$O_{diff} = 100 - (C + H + N + S) -$ ashes (dry basis).

of the coals, the contents of moisture and volatile matter as a rule increase with decreasing coal range. The volatile matter content, specifically, is significantly higher in the low level coals (Li–O, 29·9 wt%; Le–O, 34·9 wt%) than in the high level coals (A–O, 8·5 wt%; B–O, 18·5 wt%). Moreover, the ash content is very high in all coals, which is in accordance with the objectives of this work. It should be noted that the Spanish coals, as one of their main characteristics, possess a very high content of mineral matter, which usually fluctuates between 35 and 45 wt% and that rarely is lower than 30 wt% (Ministerio de Industria y Energía 1979). In any event, the ash content in the four coals used in this study falls inside the range, the power stations need to accept coal (35–45 wt%) (Radamacher and Hovernath 1959), except in C–O. The fixed carbon content, as obtained by difference, depends on the contents of moisture, ashes, and volatile matter. It is much higher in A–O than in B–O, Li–O, and Le–O.

In table 2 are also given data of the elemental analyses for the coals. The variation of the elementary composition is usually in accordance with their category. Thus, generally, the carbon content decreases with decreasing rank and hydrogen and oxygen contents increase. For A–O the carbon content is very similar to the fixed carbon content, while for the rest of the coals (particularly Le–O) they are quite different. These results are in line with the different volatile contents of the coals. Regarding the other data of the elemental analysis, the sulphur content of Li–O is as high as 5·7 wt% in Li–O, which is worth noting. The sulphur content is also significantly greater in Li–O than in A–O and B–O. The nitrogen content, however, is somewhat higher in A–O and B–O than in Li–O and Le–O.

3.2 *Mass changes*

Owing to the carbonization process of the coals, the release of gases such as H_2, CO, CH_4, C_2H_4, and so on, occurs. As a result, the proportion of organic matter present in the coals decreases, whereas that of inorganic matter increases. This change in the relative amounts of both fractions of the coals is of significance in this study as it would facilitate the study of the inorganic part by infrared spectroscopy. The average values of mass loss produced in the carbonization of coals are set out in table 3. The mass loss varies as follows: Le–O > Li–O > B–O > A–O. That is to say, it increases with decreasing coal

Table 3. Mass loss (wt%) produced in the carbonization and demineralization treatments of coals.

Sample	Carbonization	HCl	HF
A–O	12·2	11·7	8·3
B–O	20·6	5·5	7·4
Li–O	30·6	13·2	47·9
Le–O	36·7	20·0	40·1

rank, which agrees with the variation of the volatile matter content (table 2) for various coals. Actually, the mass loss is only a little higher than the volatile matter content, the existing differences between these amounts being likely related to the unequal heating conditions used in the heat treatment of coals.

Usually, the mass loss associated with the demineralization treatment of coals with HF is much higher than in HCl as the former acid is a more effective chemical agent than the latter. Thus, HF can attack low reactivity mineral components such as quartz, which is not affected by HCl. As inferred from table 3, it is so for Le–O and especially for Li–O (notice that for this coal the mass loss amounts to 47·9 wt% for HF, whereas for HCl it is only of 13·2 wt%, this being low in relative terms). For the couple A–O and B–O, however, the mass loss is rather similar, regardless of the acid used (for A–O, in fact, it is even somewhat higher when using HCl). The magnitude of the mass loss produced in the treatments of coals with acids should be influenced not only by the chemical composition of the inorganic fraction but also by a number of factors as their porous texture that should determine the accessibility of the reaction sites (i.e. components of mineral matter) to the reactants. This appears to be more hindered in A–O and B–O than in Li–O and Le–O as the mass loss is much smaller in both high rank coals, particularly in B–O. Surprisingly, the treatment of Li–O and Le–O with HF gives rise to a higher mass loss than their ash content (table 2). In this connection the composition changes that may occur both in the determination of ashes (i.e. inorganic components of the coals transform into oxides) and also in the treatments of these coals with HF should be taken into account. These treatments may further lead to formation of colloidal like particles that, when washed to remove the fluorides present in the residual solid, may be filtered, thus contributing to the mass loss.

3.3 *FT–IR spectroscopy*

The spectral analysis for the starting carbons and their carbonization and demineralization products will be based upon the following points:

– Both the organic and inorganic parts of the samples contribute simultaneously to the absorption of radiation in the infrared region of the electromagnetic spectrum, to a different extent depending on coal category and on the thermal or chemical treatment effected to it.

– The mineral matter content is quite high in all coals and increases after their carbonization. Nearly all coals contain aluminosilicates (i.e. Al atoms replace some of the Si atoms in the silicate structure, AS), such as kaolinite, illite, and so on, which are usually their most predominant minerals (Speight 1990). Other principal minerals in coal are quartz (Q), carbonates (CA), sulphides, and others (e.g. rutile) (Unsworth *et al* 1991).

– The organic matter (OM) content increases after demineralization of the coals, being higher for the low rank coals (Li–O and Le–O) than for the high rank coals (A–O and C–O).

3.3.1 *Study of starting coals*

3.3.1a *Spectrum of A–O:* The bands displayed by this spectrum (figure 1) have been assigned to stretching or bending vibrations in water, carbonates, aluminosilicates, and quartz (table 4). The band at 3624 cm^{-1} and the peak located at a higher frequency value are connected with n(O–H) vibrations in hydroxyl groups of aluminosilicates (Dixon and Weed 1979). The band at 3427 cm^{-1}, however, is attributable to the n(O–H) vibration in loosely adsorbed water molecules, as the band associated with
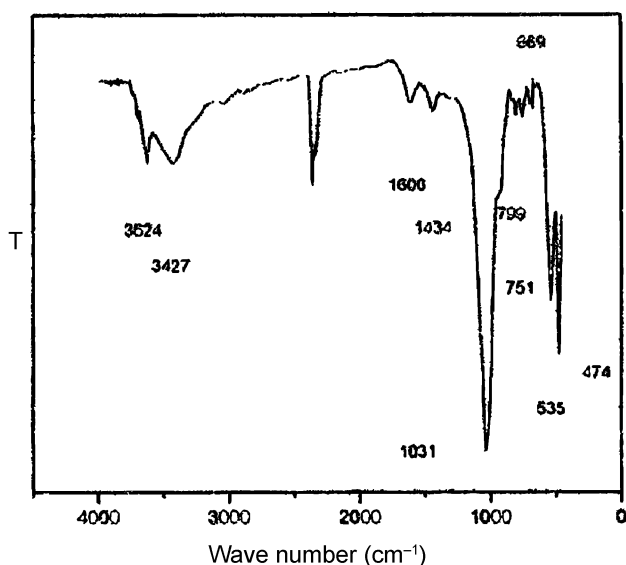

Figure 1. FT–IR spectrum of A–O.

Table 4. FT–IR spectrum of A–O. Position and assignment of bands.

Wave number (cm^{-1})	Assignment
3624	n(O–H), AS
3427	n(O–H), water
1606	d(O–H), water
1434	n(C–O), Ca
1031	n(Si–O–Si), AS
1014	n(Si–O–Al), AS
799	n(Si–O), Q
750	n(Si–O–Al), AS
699	n(Si–O–Mg), AS
651	n(Si–O), AS
535	d(Si–O–Al), AS
474	d(Si–O), AS; Q

water molecules tightly bonded to the mineral surface as a monolayer (e.g. in montmorillonite) or in mineral with crystal water (e.g. vermiculite) appears at 3250–3200 cm^{-1}. Also, water present in the small pores of the mineral particles gives rise to a band at 3220 cm^{-1} (Van der Mare and Beutelspacher 1976).

The band at 1434 cm^{-1} has been ascribed (Herzberg 1945) to the n_3 (doubly degenerate asymmetric stretching) vibration of the C–O bond in the plane structure of carbonate minerals. The bands associated with n_2 (non-degenerate out of plane bending) and n_4 (doubly degenerate planar bending) vibrations are quite narrower and located at lower wave numbers. These band positions depend on a number of factors including radius, mass and electro negativity of the single cations. Another factor is the structural arrangement (coordination) of the other components in the crystal against the CO_3^{2-} ion (Van der Mare and Beutelspacher 1976). The position of the v_3 band in the spectrum of A–O is compatible with the presence in this coal of a carbonate belonging structurally to the dolomite group, viz. dolomite, ankerite, and so on (Van der Mare and Beutelspacher 1976). For dolomite, specifically, the band due to the n_2 vibration should be located at 882 cm^{-1} and the band caused by the n_4 vibration at 728 cm^{-1}.

The identification of the infrared bands in the spectra of silicates such as clay minerals remains very difficult because of their complicated and non-constant composition and also because band positions can vary highly owing to isomorphous replacements. Furthermore, the mineral fraction of coal is usually a poly-component system and as a result, provided that one mineral is not predominant, the complexities of the overlapping may preclude a straightforward interpretation. Thus, the various spectral bands at 3624, 1031, 535, and 474 cm^{-1} are compatible with silicates with layer structures such as kaolinite, whereas that at 750 cm^{-1}, with muscovite (White 1971). In fact, these aluminosilicates together with quartz and ankerite were previously identified in A–O by X-ray diffraction (Alfaro-Domínguez *et al* 1998).

Between 1200 and 950 cm^{-1}, absorption of infrared radiation not only by layered silicates but also by various crystalline forms of silica, occurs (Farmer 1974). Accordingly, the strong band recorded in such a frequency range in the spectrum of A–O, resulting likely from the overlapping of several bands, is ascribable to the *n*(Si–O) vibration. Quartz causes absorption of radiation at slightly higher wave numbers (i.e. at 1172 and 1082 cm^{-1}) than 1031 cm^{-1}, both bands being weaker (Van der Mare and Beutelspacher 1976). Other characteristic bands for quartz are at 693, 512 and 460 cm^{-1} (Van der Mare and Beutelspacher 1976). A clue for the presence of quartz in A–O is the weak peak recorded at 799 cm^{-1} which, together with another peak at 778 cm^{-1}, is a feature usually noted in the spectra of quartz from different origin. In fact, this doublet has been selected for identification and quantitative estimation of quartz (Chester and Green 1968).

3.3.1b *Spectrum of B–O:* The bands displayed by this spectrum (figure 2) have been assigned as shown in table 5. The most remarkable feature in this spectrum is the shoulder recorded at 1092 cm^{-1}, which may be caused by absorption due to the *n*(Si–O) vibration in quartz. Then, according to these spectral results, the concentration of quartz is higher in B–O than in A–O. The existing differences in composition of the mineral fraction of both coals are also reflected by the mass loss produced in their demineralization with HCl and HF. Whereas the mass loss produced in the treatment with HCl is significantly lower in B–O than in A–O, in treatment with HF (i.e. it was effected to the already HCl-treated product) the mass loss is similar in both coals.

3.3.1c *Spectrum of Li–O:* Because the contents of volatile matter and oxygen are higher in Li–O than in A–O

and B–O, it can be presumed that absorption of radiation by the organic part of these coals is more significant in Li–O than in A–O and B–O. Bearing in mind this fact, the bands registered in the spectrum of Li–O (figure 3,

Table 5. FT–IR spectrum of B–O. Position and assignment of bands.

Wave number (cm^{-1})	Assignment
3696	*n*(O–H), AS
3620	*n*(O–H), AS
3413	*n*(O–H), water
1611	*d*(O–H), water
1443	*n*(C–O), Ca
1092	*n*(Si–O), AS
1033	*n*(Si–O), AS
1011	*n*(Si–O), AS
914	*n*(Al–O–H), AS
799	*n*(Si–O), Q
696	*n*(Si–O–Al), AS; *n*(Si–O), Q
537	*d*(Si–O), AS
473	*d*(Si–O), AS, Q

Table 6. FT–IR spectrum of Li–O. Position and assignment of bands.

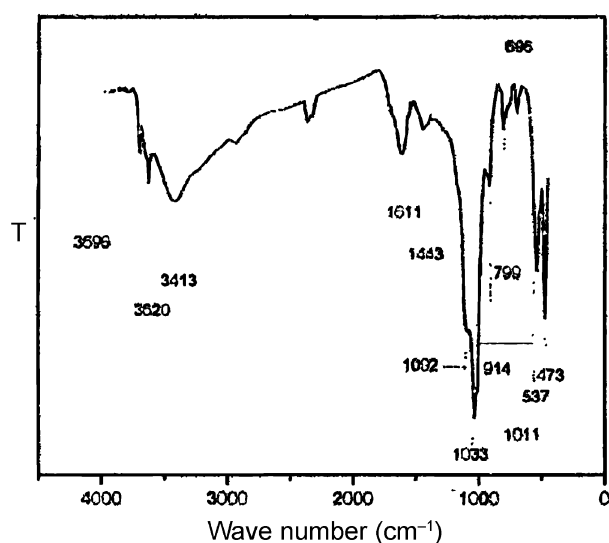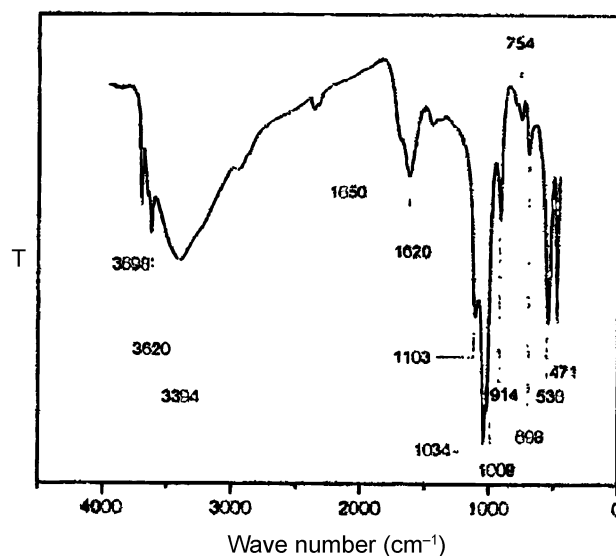| Wave number (cm^{-1})	Assignment
3698	*n*(O–H), AS
3620	*n*(O–H), AS
3395	*n*(O–H), water; *n*(O–H), OM
1650	*n*(C=O), OM
1620	*d*(O–H), water; *n*(C=C), OM
1103	*n*(Si–O), AS
1034	*n*(Si–O), AS; *n*(C–O), OM
1009	*n*(Si–O), AS
914	*n*(Al–O–H), AS; *d*(C–H), OM; *d*(OH), OM
754	*n*(Si–O–Al), AS
698	*n*(Si–O–Al), AS
471	*d*(Si–O), AS, Q

Figure 2. FT–IR spectrum of B–O.

Figure 3. FT–IR spectrum of Li–O.

table 6) at 3394, 1650, 16020, and 1034 cm^{-1} have been attributed to stretching vibrations in oxygen functional groups or in atomic groupings belonging to the chemical structure of the coal. Probably, the organic fraction will contribute as well to the absorption of infrared radiation in the frequency range between 900 and 690 cm^{-1} owing to d(C–H) (in-plane) and d(C–H) (out-of-plane) vibrations, though it is hard to assure as in this spectral region band overlappings are likely to occur.

3.3.1d *Spectrum of Le–O:*   Although the spectra of Le–O (figure 4, table 7) and Li–O as a whole are similarly shaped, they show great differences concerning the intensity of most spectral features, but especially those caused by absorption involving the organic part of the coals. Thus, the bands and shoulders recorded at 3407, 1699, 1619, 1592, and 1402 cm^{-1} in the spectrum of Le–O are much stronger than in Li–O. In fact, the band at 1402 cm^{-1}
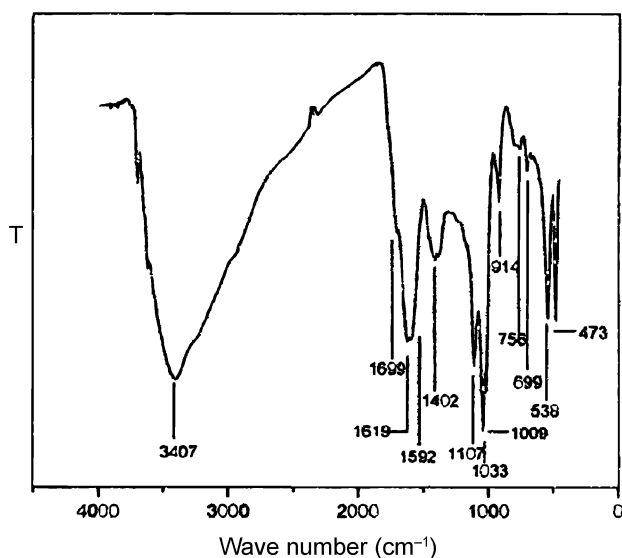
Figure 4.   FT–IR spectrum of Le–O.

Table 7.   FT–IR spectrum of Le–O. Position and assignment of bands.

Wave number (cm^{-1})	Assignment
3407	n(O–H), water, OM
1699	n(C=O), OM
1619	n(C=C), OM
1592	v(C=C), OM
1402	d(O–H), OM; n(C–O), OM
1107	n(Si–O), AS
1033	n(Si–O), AS; v(C–O), OM
1009	n(Si–O), AS; n(C–O), OM
914	n(Al–O–H), AS; d(C–H), OM; d(OH), OM
756	n(Si–O–Al), AS
699	n(Si–O–Al), AS
538	d(Si–O), AS
473	d(Si–O), AS; Q

is even hardly visible in the spectrum of Li–O. As expected, as leonardites occupy an intermediate position between the ranks of peat and lignite, these results confirm that the degree of humification (i.e. the process by which humus is formed; humus is de residue left when bacteria and fungi biodegrade plant material) (Manahan 1994) is quite larger in Le–O than in Li–O. Besides, the content of organic matter is higher in Le–O, as indicated by data of the proximate analysis obtained for both coals (table 1). Thus, the carbon content is higher in Le–O, and hence its content of mineral matter is lower for this coal. This is also evident from the spectra of Li–O and Le–O as the bands situated below ≈ 1100 cm^{-1}, which have been associated with quartz and aluminosilicates, are stronger in Li–O than in Le–O.

With the purpose of comparison, the spectra registered for the four starting coals have been plotted all together, using the same scale in the ordinate axis, in figure 5. In this way, information in qualitative and quantitative terms can be obtained for both fractions of the coals. It follows that the spectra display a very similar shape. However, there is a marked decrease of their infrared intensities by the order: Le–O > Li–O > B–O > A–O. If one takes into account that the content of mineral matter is very high in all coals (see the ash content in table 2), but especially in B–O, and that the contents of functional groups and structure being infrared active must be higher in Le–O, the spectral results denote that A–O is the least sensitive coal to the analysis by FT–IR spectroscopy, the opposite being true of Le–O.

3.3.2 *Study of the carbonized products*

3.3.2a *Spectrum of A–C:*   The band recorded above 3400 cm^{-1} in this spectrum (figure 6) is stronger than in
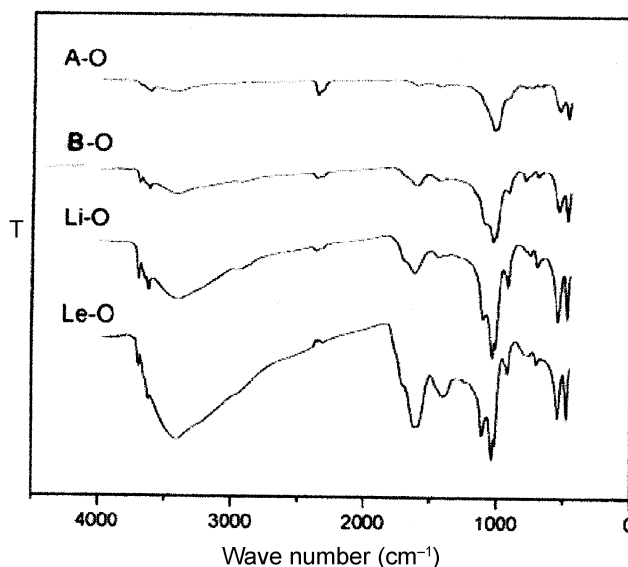

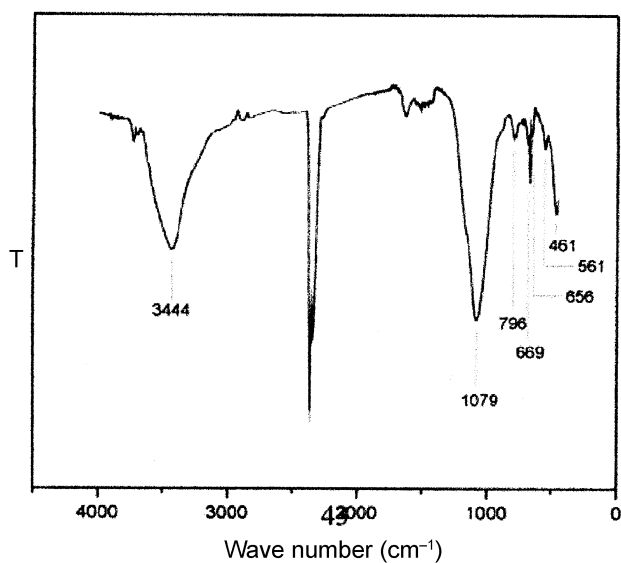**Figure 5.**   FT–IR spectra of the starting coals.

Figure 6. FT–IR spectrum of A–C.

Figure 7. FT–IR spectrum of B–C.

the spectrum of A–O. It demonstrated that such a band, as assigned above to n(O–H) vibrations, is not related to organic matter since, otherwise, it should be weaker in A–C than in A–O or even have disappeared from the spectrum of the carbonized product.

The increase of the content of mineral matter in A–C is in line with the widening produced in the band centred at 1079 cm^{-1}, which in the spectrum of A–O is located at 1031 cm^{-1}. Thus, the band shift to higher frequencies is compatible with a greater contribution to energy absorption in this region of the spectrum by quartz in A–C than in A–O.

Finally it is also remarkable the disappearance from the spectrum of A–C of the band recorded at 1434 cm^{-1} in the spectrum of A–O. This band has been assigned to the n_3 vibration of the C–O bond in carbonates. Therefore, the spectral results point out that the carbonate present in A–C decomposes thermally to form the corresponding metallic oxide and carbon dioxide that releases as a gaseous reaction product. This behaviour was to be expected as the decomposition temperature of carbonates is lower (e.g. for $MgCO_3$, 400°C) than the carbonization temperature of A–O (i.e. 1000°C).

3.3.2b *Spectrum of B–C:* The main differences between the spectra of B–O (figure 2) and B–C (figure 7) concern the regions corresponding to vibrations of the O–H and Si–O bonds. The thermal treatment of B–O seems to result in a decrease in the concentration of OH groups and, besides, in an increase in the concentration of quartz as compared to that of the aluminosilicates. In this connection notice that the peak located at 1033 cm^{-1} in the spectrum of B–O changes its position to 1086 cm^{-1} in the spectrum of B–C.
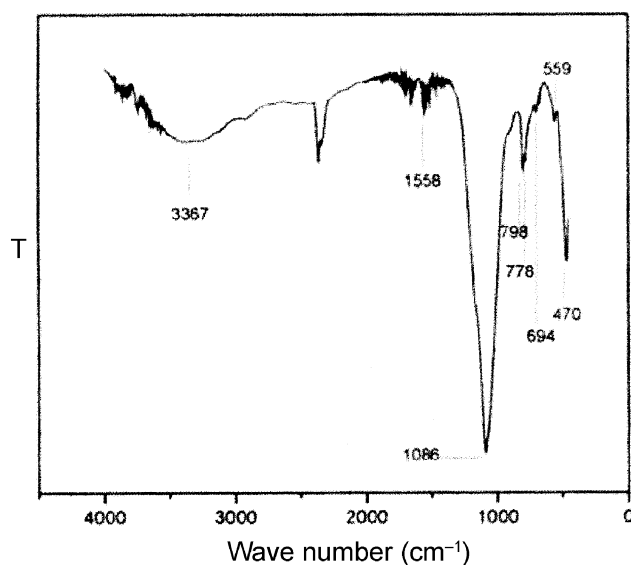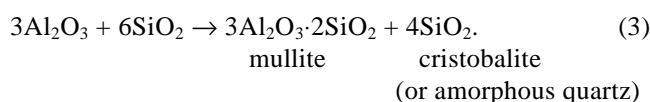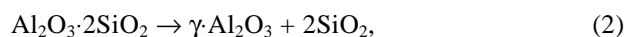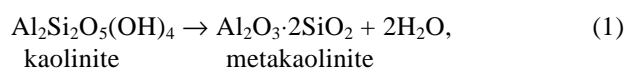
The reactions that may take place involving aluminosilicates in B–O due to thermal treatment at high temperatures are

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O, \qquad (1)$$
$$\text{kaolinite} \qquad\quad \text{metakaolinite}$$

$$Al_2O_3{\cdot}2SiO_2 \rightarrow \gamma{\cdot}Al_2O_3 + 2SiO_2, \qquad (2)$$

$$3Al_2O_3 + 6SiO_2 \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 4SiO_2. \qquad (3)$$
$$\text{mullite} \qquad \text{cristobalite}$$
$$\text{(or amorphous quartz)}$$

Concerning the thermal decomposition of kaolinite it has been reported previously (Büchner *et al* 1989) that this aluminosilicate OH-group splits off at 400 to 600°C forming metakaolinite which is stable up to 950°C. At temperatures ≥ 1150°C cristobalite and mullite are formed in the form of flakes (so-called primary mullite) by way of a spinel-type intermediate phase. Also it has been proposed (Unsworth *et al* 1991) that kaolinite loses water at ≈ 400°C to form metakaolinite, which in turn disproportionates at ≈ 900°C to form mullite and amorphous quartz. According to the literature (Van der Mare and Beutelspacher 1976), characteristic bands in the infrared spectrum of mullite are situated at 1175, 1120, 905, and 815 cm^{-1}.

3.3.2c *Spectrum of Li–C:* The main difference between the spectra of Li–O (figure 3) and Li–C (figure 8) is the band recorded at 1081 cm^{-1} in Li–C, while in Li–O a peak at 1034 cm^{-1} and two shoulders at 1103 and 1009 cm^{-1} appear. These results are also compatible with the transformation, by heating effect, of aluminosilicates
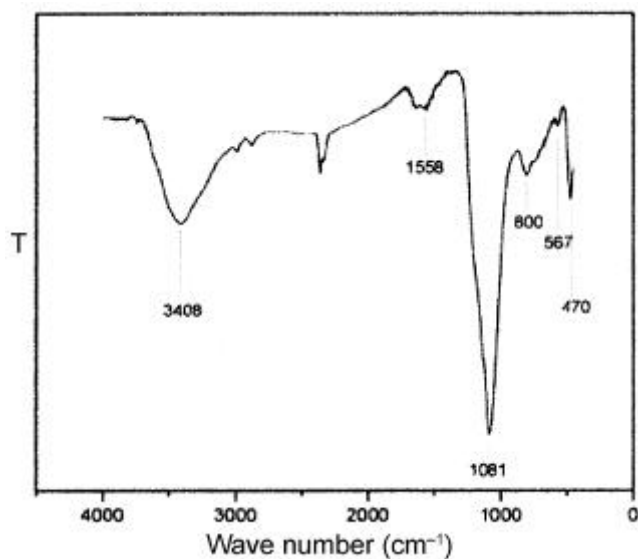
Figure 8. FT–IR spectrum of Li–C.

Figure 9. FT–IR spectrum of Le–C.

present in Li–O into some polymorphic form of silica. This is further supported by the complete absence from the spectrum of Li–C of the narrow peaks located at 3698 and 3620 cm^{-1} in the spectrum of Li–O, which have been assigned to n(O–H) vibrations in aluminosilicates. Moreover, the bands shown in the spectrum of Li–O at wave numbers < 950 cm^{-1} either are weaker in the spectrum of Li–C or even disappear from it.

Also it is worth noting that in the spectrum of Li–C is registered the relatively broad band at 1550 cm^{-1} as in this spectral region the absorption of infrared radiation due to skeletal vibrations in aromatic rings occurs. The fact that the content of aromatic structure is higher in Li–C than in Li–O (as a result, its presence can be detected in Li–C but not in Li–O), as expected, is attributable to the carbonization process of Li–O that not only produces the release of volatile matter from the coal, thus leading to a decreased organic content in the resultant product, but also aromatization of remaining organic matter (Gómez-Serrano *et al* 1996). When heating lignocellulosic materials, at least, the main chemical changes in their organic part and in the mass of sample, take place usually at temperatures below 600°C.

3.3.2d *Spectrum of Le–C:* As can be seen (figures 4 and 9), most of the strong bands present in the spectrum of Le–O are absent from the spectrum of Le–C. Besides, as for the other three coals the overlapped band with three peaks at 1107, 1033 and 1009 cm^{-1} recorded in the spectrum of Le–O is not displayed by the spectrum of Le–C. This spectrum, instead, only shows a single band at 1082 cm^{-1}. At frequencies below ≈ 900 cm^{-1}, also, the number, position and intensity of the bands are different.

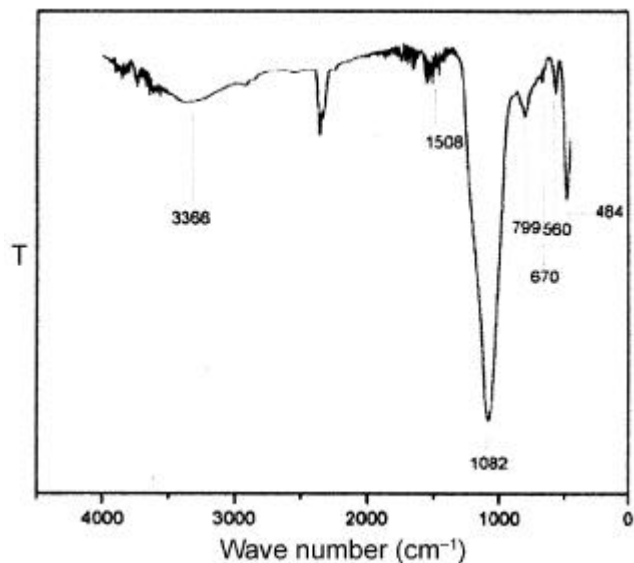From these spectral results it becomes clear that the carbonization of Le–O produces dramatic changes in the organic part of this coal. The only feature in the spectrum of Le–C that may be associated with organic structures of Le–C is the wide band located at 3366 cm^{-1}, which is possibly caused by n(O–H) vibrations of phenolic hydroxyl groups, as the fractions of these oxygen functional groups are quite stable thermally (Jankowska *et al* 1991), and the weak and poorly defined band at 1508 cm^{-1}, which may be due to n(C=C) vibrations in aromatic rings. Ether type structures are also stable (Jankowska *et al* 1991), and absorb energy between 1215 and 1050 cm^{-1} owing to the n(C–O–C) vibration (Brand and Eglinton 1965). On the other hand, the heat treatment of Le–O also affects its mineral fraction, as suggested by the modifications noticed in the spectra at wave numbers lower than 1300 cm^{-1}.

In short, the main feature exhibited by the spectra of the four carbonized samples is the band recorded around 1080 cm^{-1}, which is ascribable to n(Si–O) vibrations in inorganic components such as quartz, aluminosilicates (i.e. if some of them would remain unaffected after the heat treatment of the starting coals) and the products of their thermal transformation. The fact that the band is located at close values of the wave numbers appears to indicate that the same chemical components are present in all carbonized products. As far as their total content is concerned, when the spectra are plotted altogether by using the same scale in the ordinate axis (figure 10), it follows that this content varies by the order: Le–C π B–C $>$ Li–C $>$ A–C which will depend both on the extent of removal of volatile matter from the starting coals and on their mineral contents.

3.3.3 *Study of demineralized products*

3.3.3a *Spectrum of A–D:* As inferred from figures 1 and 11, when A–D is treated with HCl and HF the mineral fraction undergoes severe modifications. Thus, the spectra of A–O and A–D display quite different shapes. Some pronounced features in the spectrum of A–D, which are not exhibited by the spectrum of A–O, are the shoulder at 1697 cm^{-1} and the band at 1578 cm^{-1}. Besides, the band located in the frequency range between 1300 and 900 cm^{-1} is much broader in the spectrum of A–D and its strongest peak shifts to significantly higher frequencies (i.e. at 1238 cm^{-1}, instead of at 1031 cm^{-1}). These features denote the presence of C=O groups, C=C bonds and struc-
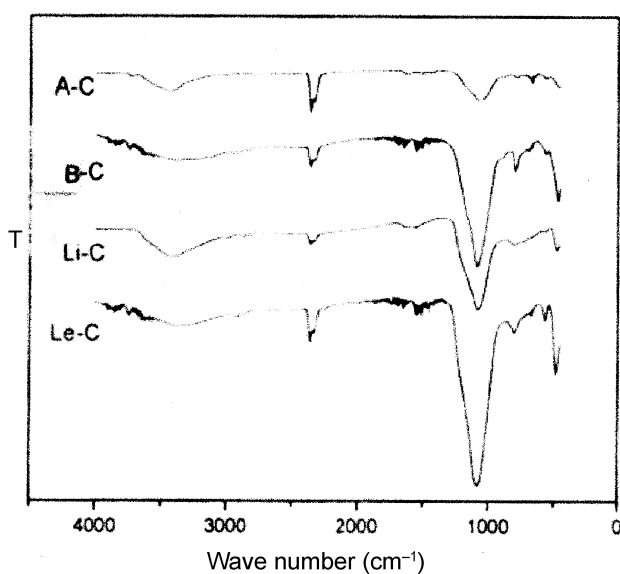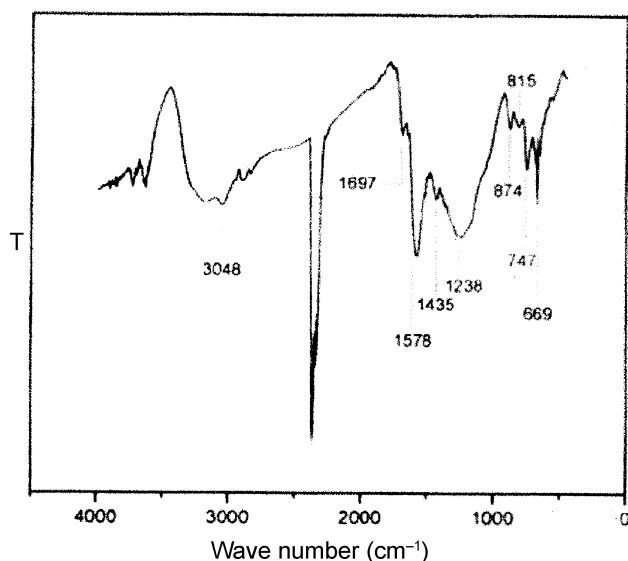
tures with C–O bonds in A–D, which is not revealed by the spectrum of A–O.

The band recorded in the spectrum of A–O at 3427 cm^{-1}, which is due to n(O–H) vibrations, is not registered in the spectrum of A–D, which proves again that it is not associated with OH groups belonging to the organic fraction of the coal. Moreover, the fact that band situated between 1300 and 900 cm^{-1} is broad suggests that the absorption of infrared radiation in this spectral region will contribute not only to ether type structures but also Si–O bonds in quartz and aluminosilicates still remaining in A–D after the acid treatments of A–O.

Surprisingly, the band at ≈ 1435 cm^{-1} in the spectrum of A–O is also shown as a peak in the spectrum of A–D. It has been connected with the presence of carbonate minerals in A–O. For A–D, however, such a band deserves a different assignment as the carbonates are soluble in HCl. Thus it is related to the organic fraction of A–D or, otherwise, the carbonates are not completely removed from A–O by treatment with HCl.

The above results suggest that only after demineralization of the coal, study of its organic fraction is feasible by FT–IR spectroscopy, which is an analysis tool that then provides valuable information concerning the identification of the oxygen functional groups and structures present in coal.

3.3.3b *Spectrum of B–D:* The spectrum of B–D (figure 12) shows a number of absorption bands at 3396, 1710, 1614, 1436, 1246 cm^{-1}, and so on, which are assigned to vibration modes in its organic fraction and also in the remaining inorganic one after the acid treatments of B–O. Thus, the band at 3396 cm^{-1} may be connected with phenolic hydroxyl groups of OM and also with water adsorbed. Likewise, to the absorption of energy
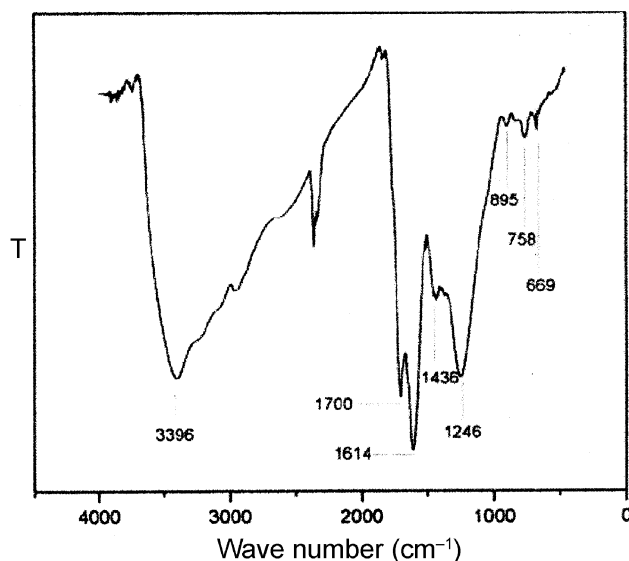

Figure 10. FT–IR spectra of the carbonized products.

Figure 11. FT–IR spectrum of A–D.

Figure 12. FT–IR spectrum of B–D.

around 1436 cm^{-1}, it may contribute C=C, O–H and C–O bonds of OM and C–O bond of Ca. Moreover, the band at 1246 cm^{-1} may arise from the absorption due to C–O–C bonds in ether type structures of OM and to Si–O bonds of quartz and aluminosilicates. However, this band is centred at a significantly higher frequency in B–D than in B–O (1033 cm^{-1}), which denotes a greater absorption by the organic fraction of B–D than by its inorganic fraction.

3.3.3c *Spectrum of Li–D:* The spectrum of Li–D (figure 13), as compared to the spectrum of Li–O (figure 3), mainly shows the appearance of the bands at 2927 cm^{-1} (i.e. this feature is ascribable to the asymmetric vibration mode of methylene groups) and 1269 cm^{-1} and a much smaller number of bands below 950 cm^{-1} (the broad band centred at 640 cm^{-1} may be caused by bending (out-of-plane) of the O–H bond). Also, the sharp band at 1009 cm^{-1} in the spectrum of Li–O becomes an almost imperceptible shoulder in the spectrum of Li–D. Therefore, significant bands that have been connected above with mineral matter of the coal either greatly decreases in intensity or are not registered in the spectrum of Li–D. These results reflect the large extent to which the demineralization of Li–O occurs by treatment of this coal with HF (i.e. the mass loss is as high as 47·9 wt%, table 3). Moreover, they also support the above band assignments made for the starting coals, which is worth noting.

3.3.3d *Spectrum of Le–D:* The spectrum of Le–D (figure 14) is also dissimilarly shaped to that of Le–O. Thus, the peak at 1714 cm^{-1} in the former is very strong, whereas in the latter only a scarcely visible shoulder at 1699 cm^{-1} is detected. According to the peak position and intensity for Le–D, this chemically treated product of

Le–O contains carboxylic acid groups, the content of which is further very high. However, it is evident that from the spectrum of Le–O valuable information concerning both types of C=O groups present in the material and their concentration cannot be obtained.

Below 1300 cm^{-1}, the sharp peak located at 1033 cm^{-1} in the spectrum of Le–O shifts to 1252 cm^{-1} in the spectrum of Le–D, in which only remains a weak shoulder at 1033 cm^{-1}. Besides, the intensity and the number of bands recorded at frequencies lower than 900 cm^{-1} are quite smaller in the spectrum of Le–D. These results, as for Li–O, also give one idea of the effectiveness of the acid treatments to demineralize Le–O. In the case of this
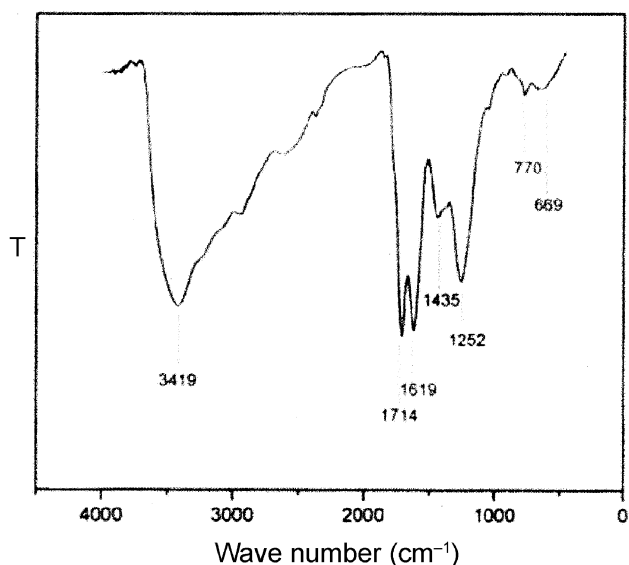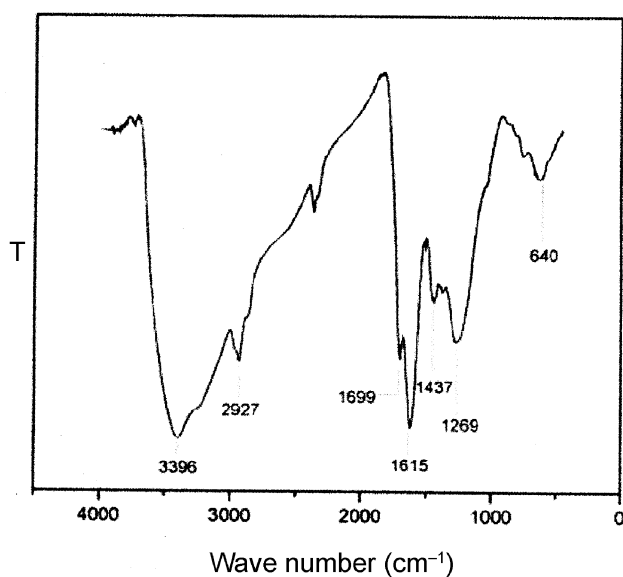

Figure 14. FT–IR spectrum of Le–D.

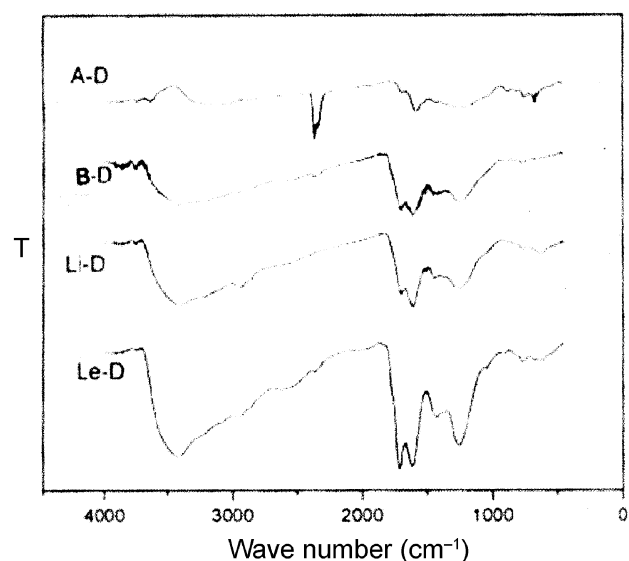**Figure 13.** FT–IR spectrum of Li–D.

Figure 15. FT–IR spectra of the demineralized products.

coal, in fact, the mass loss is 20 wt% for HCl and 40·1 wt% for HF, which are very large values.

The spectra registered for A–D, B–D, Li–D and Le–D are plotted in figure 15. As can be seen, all spectra display a similar shape but the band intensities are different for the four products. Therefore, they must possess a similar chemical structure in their organic fraction but with different contents of surface groups and structures that contribute to the absorption of infrared radiation in various spectral regions, which depend on the rank of the starting coals. Such contents vary by the following order: Le–D π Li–D > B–D > A–D.

3.4 *Optimization of FT–IR spectroscopy*

Coal, though mainly amorphous, is slightly crystalline, which makes it opaque and restricts the transmission/absorption of electromagnetic radiation. Hence, choosing an adequate coal : KBr ratio and mass, or thickness, in the preparation of disks may be an important factor for a more proper analysis of coal by FT–IR spectroscopy. Accordingly, using A–O only as an example, two further series of disks were prepared (see tables 8 and 9). The infrared spectra registered for the resultant disks are shown in figures 16 and 17. It follows that the intensity of infrared absorption in the whole frequency range between 4000 and 450 cm^{-1} significantly decreases with

Table 8. Disks prepared by varying the coal : KBr ratio (mass, 150 mg).

Ratio	1 : 300	1 : 400	1 : 500	1 : 600
Preparation number	1	2	3	4
Notations	A–O–1	A–O–2	A–O–3	A–O–4

decreasing coal : KBr ratio. It means that a larger degree of the dilution of the coal in KBr reduces the extent to which the absorption of radiation occurs. The influence of the disk thickness on the absorption of energy is shown by the fact that this first greatly increases with increasing thickness and then remains practically unaffected. Then, for comparison purposes in the case of A–O it would be advisable to use the same coal : KBr ratio and a high thickness for the disks. The influence of the coal rank and the carbonization and demineralization treatments of the coals on the application of the FT–IR spectroscopy will be the object of subsequent investigations.

4. Conclusions

The FT–IR spectra registered for the four starting coals are very similarly shaped, though with different intensity

Table 9. Disks prepared by varying the thickness (coal : KBr ratio, 1 : 400).

Mass (mg)	100	150	200	250	300
Preparation number	1	2	3	4	5
Notations	A–O–1	A–O–2	A–O–3	A–O–4	A–O–5

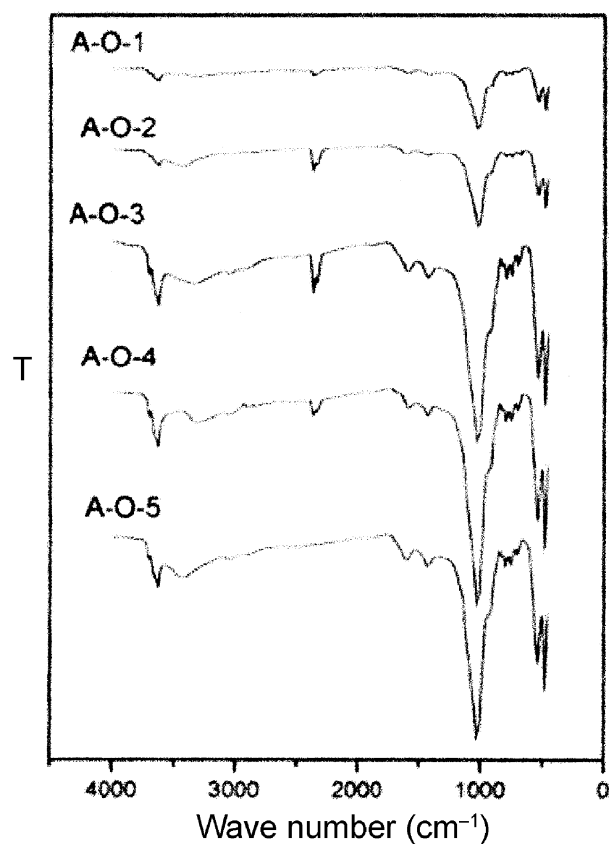**Figure 16.** FT–IR spectra for A–O. Disks prepared by varying the coal : KBr ratio.

Figure 17. FT–IR spectra for A–O. Disks prepared by varying the thickness.

of infrared absorption in the whole spectral range between 4000 and 450 cm^{-1}. Such an intensity increases with decreasing coal rank. These results indicate that, in general, all coals possess the same mineral components and organic functional groups and structures. However, the sensitivity to the analysis by FT–IR spectroscopy appears to be less with increasing coal rank.

For the high rank coals the spectra recorded intense bands that have been assigned to vibration modes in mineral components as quartz and aluminosilicates, such as kaolinite. For the low rank coals, the spectra display as well some further bands, being also quite intense, which have been ascribed to bond vibrations in functional groups and structures belonging to their organic fraction.

The carbonization of the starting materials produces remarkable changes in the composition of their mineral fraction. As a result, the content of quartz increases and the content of aluminosilicates decreases in the products obtained. Also, the thermal decomposition of carbonates occurs. The organic part dramatically changes, mainly for lignite and leonardite, as most of the organic structures and functional groups present in the coals are not stable thermally. The demineralization treatment of the coals is usually more effective for HF than for HCl. The mass losses are higher for lignite and leonardite than for anthracite and bituminous coal.

The infrared spectroscopy allows the analysis of both inorganic and organic fractions of the coals. The carbonization and demineralization of the coals makes easy the analysis of their inorganic and organic fraction, respectively.

In the optimization study of the application of FT–IR spectroscopy it has been found that for anthracite coal : KBr ratio used in the preparation of disks and disk thickness influence the intensity of infrared absorption.

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