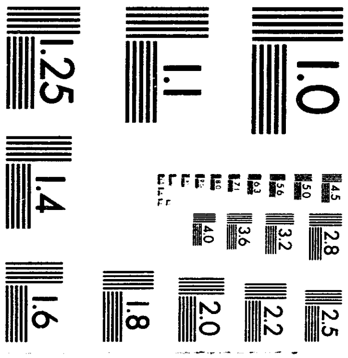
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OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
DE-FG22-90PC90287

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TECHNICAL PROGRESS REPORT (December 31, 1993)

RESEARCH OBJECTIVES

The objective of this research is to develop a mechanistic understanding of the oxidation of coal and coal pyrite, and to correlate the intrinsic physical and chemical properties of these minerals, along with changes resulting from oxidation, with those surface properties that influence the behavior in physical cleaning processes. The results will provide fundamental insight into oxidation, in term of the bulk and surface chemistry, the microstructure, and the semiconductor properties of the pyrite.

During the thirteenth quarter, wet oxidation tests were done on coal samples from the Pennsylvania State Coal Bank. As-received and oxidized coal samples were studied by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy to detect functional groups that might be responsible for changing the hydrophobicity of coal samples.

EXPERIMENTAL METHODS AND RESULTS

a.- Sample Characterization

Coals with different rank and sulfur content, obtained from the Pennsylvania State Coal Bank, were studied. Table I shows the proximate and sulfur analysis of the coals studied.

b.- Wet Oxidation Studies

Coal samples from the Pennsylvania State Coal Bank were oxidized for 5 hours at room temperature using 10% H_2O_2 at pH 1.0, 1.0 M HNO_3 or 0.05 M $Fe_2(SO_4)_3$ at pH 1.0. Details of the experimental procedure used in the wet oxidation tests were provided in our September 30, 1993 report, along with results of ion-exchange analysis and film flotation tests on as-received and oxidized coal samples. Table II shows the weight percentage of carboxylic and phenolic group oxygen generated by oxidation with different treatments, as determined by ion-exchange. DRIFT spectroscopic analysis was done on as-received and oxidized samples to identify different functionalities directly, to supplement the information on carboxylic and phenolic groups obtained indirectly by ion-exchange methods. The procedure for DRIFT analysis was reported in our June 30, 1993 report.

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Table I: Proximate and Sulfur Analysis of Coal Samples Studied

Penn State Coal Bank No	Origin	Rank	Proximate (dry, %)				Sulfur Forms (dry, %)			
			Ash	Volatile Matter	Fixed Carbon	Moisture (as rec'd)	Sulfatic	Org. Sulfur	Pyritic	Total
PSOC-1442	Darco Texas	Subbituminous C	11.27	67.39	21.34	32.60	0.02	0.65	0.11	0.78
PSOC-1494	Kentucky #9 Kentucky	HVB Bituminous	11.81	38.51	49.58	7.12	0.02	1.69	3.14	4.85
PSOC-1481	Upper Clarion Penn.	HVA Bituminous	8.91	39.41	51.68	1.73	0.20	1.42	3.20	4.82
DECS-12	Pittsburgh #8 Penn.	HVA Bituminous	10.25	36.02	53.73	2.40	0.01	0.73	0.38	1.12
PSOC-1527	Upper Freeport Penn.	MV Bituminous	30.44	23.25	46.31	0.46	0.05	0.34	1.63	2.02
PSOC-1516	Lower Kittanning Penn.	LV Bituminous	10.31	17.73	71.96	1.97	0.01	0.78	0.61	1.40
PSOC-1461	Mammoth Penn.	Anthracite	24.18	4.01	71.81	3.06	0.02	0.65	0.11	0.78

Table II: Weight Percentage of Carboxylic and Phenolic Group Oxygen of As-received Coal, and Coal Oxidized in Different Solutions, Determined by Ion Exchange

Coal Sample	As-received		1.0 M HNO_3		10 % H_2O_2		0.05 M $Fe_2(SO_4)_3$	
	Carboxylic %	Phenolic %	Carboxylic %	Phenolic %	Carboxylic %	Phenolic %	Carboxylic %	Phenolic %
PSOC-1442	0.99	3.23	2.20	10.50	1.10	9.10	1.80	9.50
PSOC-1481	0.81	2.84	1.87	3.87	1.02	4.12	2.81	3.97
PSOC-1527	0.25	1.22	2.10	10.50	2.20	9.10	0.80	8.00
PSOC-1461	0.11	1.47	0.26	1.42	0.92	1.61	1.40	1.81

Figures 1 and 2 show the spectra of as-received and oxidized sub-bituminous C (PSOC-1442) coal and Table III summarizes the major peaks observed, along with their intensities. The broad peak observed at about 3400.0 cm^{-1} corresponds to hydroxyl vibrations. The wavenumber of this peak was not changed by oxidation, and its intensity increased slightly. Comparison with Table II shows that although the increase in peak intensity is qualitatively consistent with an increase in carboxylic and phenolic groups, the agreement is not quantitative. The spectral range between 3000 and 2800 cm^{-1} corresponds to the alkyl group region (CH, CH_2 and CH_3). As-received coal exhibited two principal peaks at 2921.8 and 2850.9 cm^{-1}. Although these were unchanged by treatment with 10 %

Table III: DRIFT absorption peaks of as-received and oxidized sub-bituminous C (PSOC-1442) coal.

As-received		1.0 M HNO_3		10 % H_2O_2		0.05 M $Fe_2(SO_4)_3$	
Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity
3402.2	0.44	3402.2	0.49	3402.2	0.48	3402.2	0.53
2921.8	0.41	2928.9	0.43	2921.8	0.40	2921.8	0.42
2850.9	0.36	2858.0	0.37	2850.9	0.35	2850.9	0.37
1701.9	0.38	1701.9	0.49	1701.9	0.48	1701.9	0.55
1609.7	0.47	1616.8	0.53	1616.8	0.49	1616.8	0.64
1439.5	0.42	1446.6	0.49	1446.6	0.42	1446.6	0.57
1283.4	0.38	1283.4	0.52	1283.4	0.46	1283.4	0.59
1038.7	0.38	1045.8	0.43	1045.8	0.38	1045.8	0.48

H_2O_2 and 0.05 M $Fe_2(SO_4)_3$, the former shifted to 2928.9 cm^{-1} and the latter to 2858.0 cm^{-1} after treatment with 1.0 M HNO_3. The intensity of the peaks did not change, within experimental error. This contrasts with the behavior of the same coal on oxidation by air at 230°C (June 30, 1993 report, Figure 8-B), where the intensity of the alkyl peaks was significantly decreased, and indicates that wet oxidation treatments did not markedly alter the aliphatic structure of this coal. The as-received coal showed a shoulder at 1701.9 cm^{-1} and two peaks at 1609.7 and 1439.5 cm^{-1}. The shoulder at 1701.9 cm^{-1} is due to the carbonyl group in a carboxylate environment. The peaks at 1609.7 and 1439.5 cm^{-1} correspond to aromatic C=C stretching and C-H deformation, respectively. These peaks changed after all wet oxidation treatments. The most significant change is the increase in intensity of the carbonyl absorption at 1701.9 cm^{-1}, from a shoulder to a distinctive peak. Qualitatively, this is consistent with the increase in carboxylic group oxygen reported in Table II after oxidation with all three aqueous oxidants, although there is not a good quantitative agreement. It should, however, be recognized that neither the ion-exchange techniques used to determine carboxylate and phenolic oxygen analytically, nor the DRIFT technique that involves repeated reflections at the surface of the opaque coal, will sample the bulk of the coal, and there is no reason why they should both be sampling the same surface region. Moreover, the difference between the intensity of the peaks or shoulders and the background intensity at that wavelength is a better indicator of the quantity of the functional group present. The peak at 1609.7 cm^{-1}, which shifted to 1616.8 cm^{-1} after wet oxidation, appeared to be due to aromatic hydrogen substitution patterns[1]. The intensity of this peak increased after all treatments, due to the increase in adjacent oxygen-containing functional groups, which induce an asymmetry in the aromatic rings[2]. The peak at 1439.5 cm^{-1}, corresponding to an in-plane aromatic CH deformation, shifted to 1446.6 cm^{-1}, probably because of substitution by OH groups in the ring structure[1]. Also, the peak intensity only increased after oxidation by 0.05 M $Fe_2(SO_4)_3$ or 1.0 M HNO_3.

Consistent with the increase in the concentration of phenolic groups after oxidation reported in Table II, the peak at 1283 cm^{-1}, corresponding to C-O stretching (phenols) coupled with OH deformation, increased for all oxidized samples. The peak at 1038.7 cm^{-1}

Table IV: **DRIFT absorption peaks of HVA bituminous (PSOC-1481) coal, as-received and oxidized with 1.0 M HNO_3**

As-received		1.0 M HNO_3	
Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity
3453.8	0.34	3453.8	0.34
2921.8	0.36	2921.8	0.35
2858.0	0.33	2858.0	0.32
1701.9	0.28	1701.9	0.34
1609.7	0.36	1609.7	0.36
1443.0	0.36	1443.0	0.33
1191.2	0.38	1191.2	0.35
1049.4	0.35	1049.4	0.42

that corresponds to C_{al}-O-C_{al} stretching[3] (al=aliphatic) increased to 1045.8 cm^{-1} after all oxidation treatments, although the intensity was only increased by 0.05 M $Fe_2(SO_4)_3$ and 1.0 M HNO_3.

Figure 3 shows the spectra of HVA bituminous (PSOC-1481) coal, as-received and oxidized with 1.0 M HNO_3. Table IV summarizes the wavenumbers and intensities of the major peaks observed in Figure 3. The peaks observed for this bituminous coal are similar to those in Figures 1 and 2; the peak at about 3450 cm^{-1} corresponding to hydroxyl vibrations, and the peaks at 2921.8 cm^{-1} and 2858.0 cm^{-1} corresponding to the alkyl region were not changed by oxidation. Again, the most significant change was the increase in intensity of the carbonyl peak at 1701.9 cm^{-1}, due to the formation of carboxylic groups on oxidation. The peak at 1609.7 cm^{-1} was not altered by oxidation, whereas the peaks at 1443.0 cm^{-1} and 1191.2 cm^{-1} experienced a slight decrease in intensity. A peak emerged at 1049.4 cm^{-1} after oxidation; this probably has its origin in the C-O stretching of aliphatic ethers[4]. Similar spectra (not shown) were obtained for this coal oxidized with H_2O_2 and $Fe_2(SO_4)_3$.

Figures 4 and 5 show the spectra of as-received and oxidized MV bituminous (PSOC-1527) coal. Table V summarizes the principal features of these spectra. This coal showed a series of peaks at high wavenumbers, predominated by a peak at 3617.0 cm^{-1} that decreased after oxidation and shifted to 3624.1 cm^{-1} after treatment with 10 % H_2O_2. This feature is thought to be due to specific minerals (an ash analysis of this coal was not available). A similar peak has been assigned to kaolinite ($Al_2(Si_2O_5)(OH)_4$)[5,6]. The broad hydroxyl peak at 3382.9 cm^{-1} decreased in intensity after all oxidation treatments, although there was a marked increase in the concentration of surface phenolic groups measured by ion-exchange. A peak at about 3042 cm^{-1} associated to aromatic C-H stretching was present in addition to peaks corresponding to the alkyl groups (CH, CH_2 and CH_3); this is consistent with the fact that high rank coals have a more aromatic structure. The intensity of these peaks was slightly reduced by all wet oxidation procedures, however; Figure 6 shows that the same coal oxidized in air at 230°C experienced a dramatic decrease in the intensity of peaks corresponding to the alkyl groups. This confirms the fact that dry oxidation severely modifies the aliphatic structure of coal.

Table V: DRIFT absorption peaks of as-received and oxidized MV bituminous (PSOC-1527) coal

As-received		1.0 M HNO_3		10 % H_2O_2		0.05 $Fe_2(SO_4)_3$	
Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity
3617.0	0.45	3617.0	0.34	3624.1	0.38	3617.0	0.40
3382.9	0.53	3382.9	0.36	3382.9	0.40	3382.9	0.44
3042.4	0.51	3042.4	0.37	3042.4	0.38	3042.4	0.41
2928.9	0.57	2921.8	0.50	2921.8	0.51	2921.8	0.54
2858.0	0.51	2865.1	0.42	2872.2	0.42	2865.1	0.45
1652.3	0.40	1652.3	0.42	1652.3	0.42	1652.3	0.42
1609.7	0.53	1609.7	0.53	1609.7	0.55	1609.7	0.55
1453.7	0.53	1446.3	0.53	1439.5	0.57	1446.3	0.54
1191.2	0.54	1191.2	0.47	1191.2	0.53	1191.2	0.54
1099.0	0.61	1099.0	0.52	1099.0	0.63	1099.0	0.65
1028.1	0.67	1031.6	0.64	1028.1	0.77	1035.2	0.77
914.6	0.51	914.6	0.46	914.6	0.55	914.6	0.52
801.1	0.52	804.7	0.47	801.1	0.54	801.1	0.52

Figures 4 and 5 contain no carbonyl peak at about 1700 cm^{-1}. This also is inconsistent with results of ion-exchange (Table II); the analytical data indicate a significant increase in the amount of oxygen functional groups with all wet oxidation procedures that was not reflected by an increase in the peak intensity at 1700 cm^{-1}. This inconsistency is not yet understood. A small shoulder at 1652.3 cm^{-1}, associated with highly conjugated carbonyl, most probably quinone type[7,8,9], appeared in all spectra of wet oxidized coal. A small peak was present at about 1191.2 cm^{-1}, probably due to C-O stretching vibrations, mainly of ether groups[10,11] or to C-OH species[12]. The peaks at 1099.0 cm^{-1} and 1028.1 cm^{-1} are probably due to kaolinite[5,6]. In the range from 900 and 650 cm^{-1} this MV bituminous coal exhibited at least nine different peaks of medium intensity which are characteristic of out of plane aromatic C-H deformations.

Table VI: DRIFT absorption peaks of anthracite (PSOC-1461) coal, as-received and oxidized with 1.0 M HNO_3

As-received		1.0 M HNO_3	
Peak cm^{-1}	Intensity	Peak cm^{-1}	Intensity
3638.2	0.42	3638.2	0.45
3255.2	0.41	3255.2	0.45
1588.5	0.37	1588.5	0.37
1425.3	0.36	1425.3	0.36
1028.1	0.46	1028.1	0.50
801.1	0.37	801.1	0.35

Figure 7 shows the spectra of anthracite (PSOC-1461) coal, as-received and oxidized with 1.0 M HNO_3. Table VI summarizes the major features of Figure 7. Figure 7 indicates that this anthracite coal showed a more uniform adsorption in the region between 3000-1500 cm^{-1} than lower rank coals. As expected, no significant differences between both spectra were evident; this is consistent with the negligible oxidation experienced by this coal (Table II). The peak present at about 3600 cm^{-1} is attributable to kaolinite[4,5]. Two peaks are evident at 1588.5 and 1425.3 cm^{-1} corresponding to C=C aromatic stretching. The strong peak at 1028.1 cm^{-1} could correspond to the presence of kaolinite and quartz[4]. The ash of this coal was 56.5 % SiO_2 (wt% dry basis). The peaks at 1028.1 cm^{-1} and 3600 cm^{-1} were not significantly altered by any of the oxidation procedures. Peaks of medium to small intensity characteristic of out of plane aromatic C-H deformations are present between 900 and 650 cm^{-1}, consistent with the aromatic nature of anthracite coals. Similar spectra (not shown) were obtained for this coal oxidized with H_2O_2 and $Fe_2(SO_4)_3$.

DRIFT spectroscopic analysis is a sensitive technique for detecting changes in the structure of coal as a result of oxidation. A set of four as-received and oxidized coals with different ranks were characterized by DRIFT analysis; good qualitative information on the absorption of the main functionalities present in coals were obtained. The organic structural changes caused by oxidation of different coals in aqueous H_2O_2, HNO_3 or $Fe_2(SO_4)_3$ solutions were in general similar with the exception of the formation of aliphatic ethers in sub-bituminous C (PSOC-1442) and HVA bituminous (PSOC-1481) coals, and the formation of quinone type structures and aromatic ethers in MV bituminous (PSOC-1527) coal. As expected no significant differences between as-received and oxidized anthracite coal were detected. Ash constituents such as kaolinite and quartz present in MV bituminous and anthracite coals were unaltered by oxidation. In general, the most significant agreement between the results for oxidation of coals with air at 230°C and wet oxidation using different oxidizing agents was in the appearance of a band at about 1700 cm^{-1} which is normally attributable to carbonyl absorption. However, thermal oxidation at 230°C induced significant changes in the aliphatic structure of low rank coals whereas wet oxidation treatments were less severe.

c. Future Work

Flotation tests at controlled potentials and pH are planned, to correlate coal cleaning with the electrochemical work done earlier in this project. The influence of electrode potential on the surface properties of pyrite will be tested using contact angle measurements on polarized coal pyrite electrodes.

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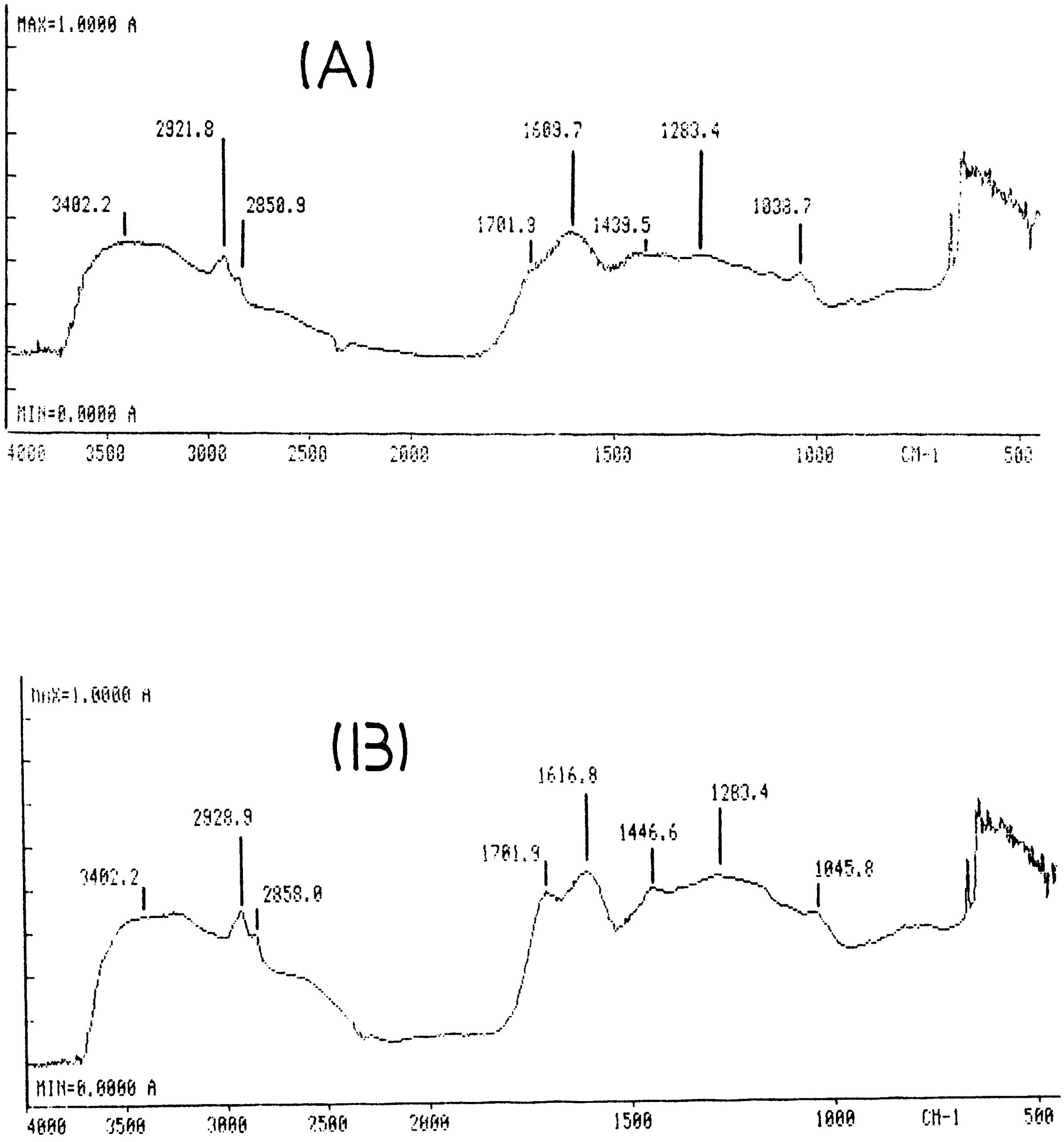

Figure 1: DRIFT spectra of sub-bituminous C (PSOC-1442) coal; (A): as-received; (B): oxidized with 1.0 M HNO_3 for 5 hours at room temperature

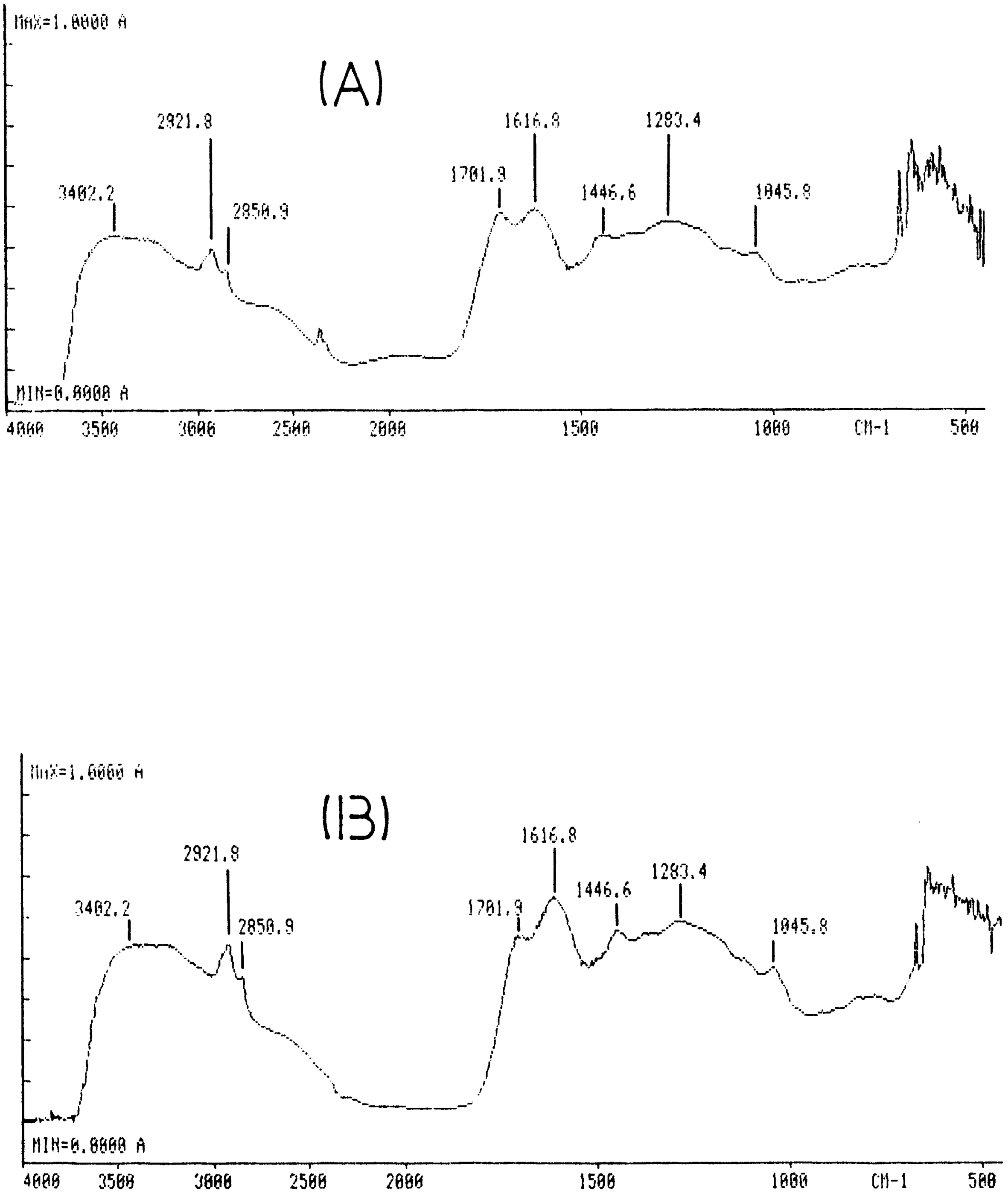

Figure 2: DRIFT spectra of sub-bituminous C (PSOC-1442) coal; (A): oxidized with H_2O_2; (B):oxidized with 0.05 M $Fe_2(SO_4)_3$ for 5 hours at room temperature

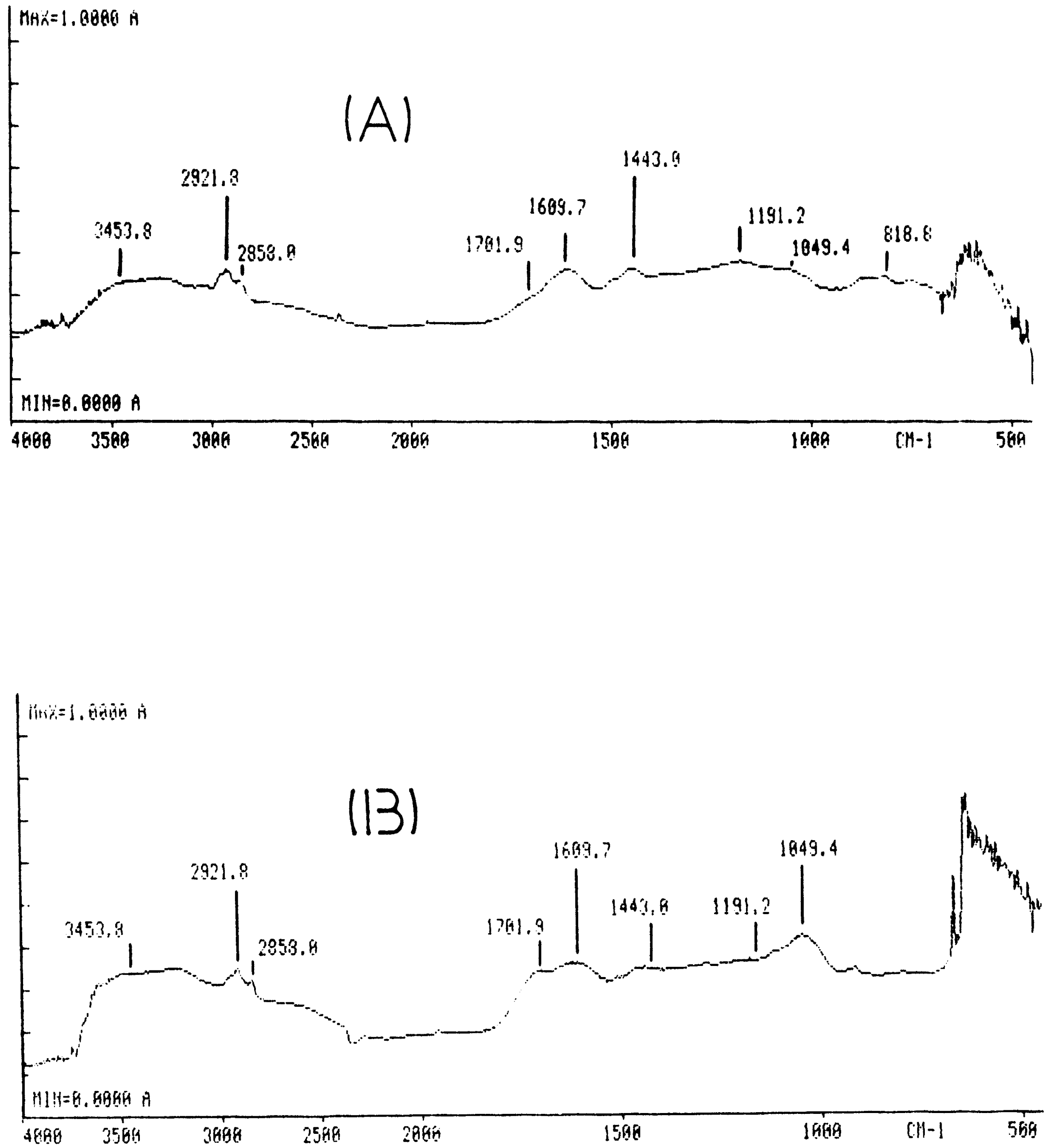

Figure 3: DRIFT spectra of HVA bituminous C (PSOC-1481) coal; (A): as-received; (B): oxidized with 1.0 M HNO_3 for 5 hours at room temperature

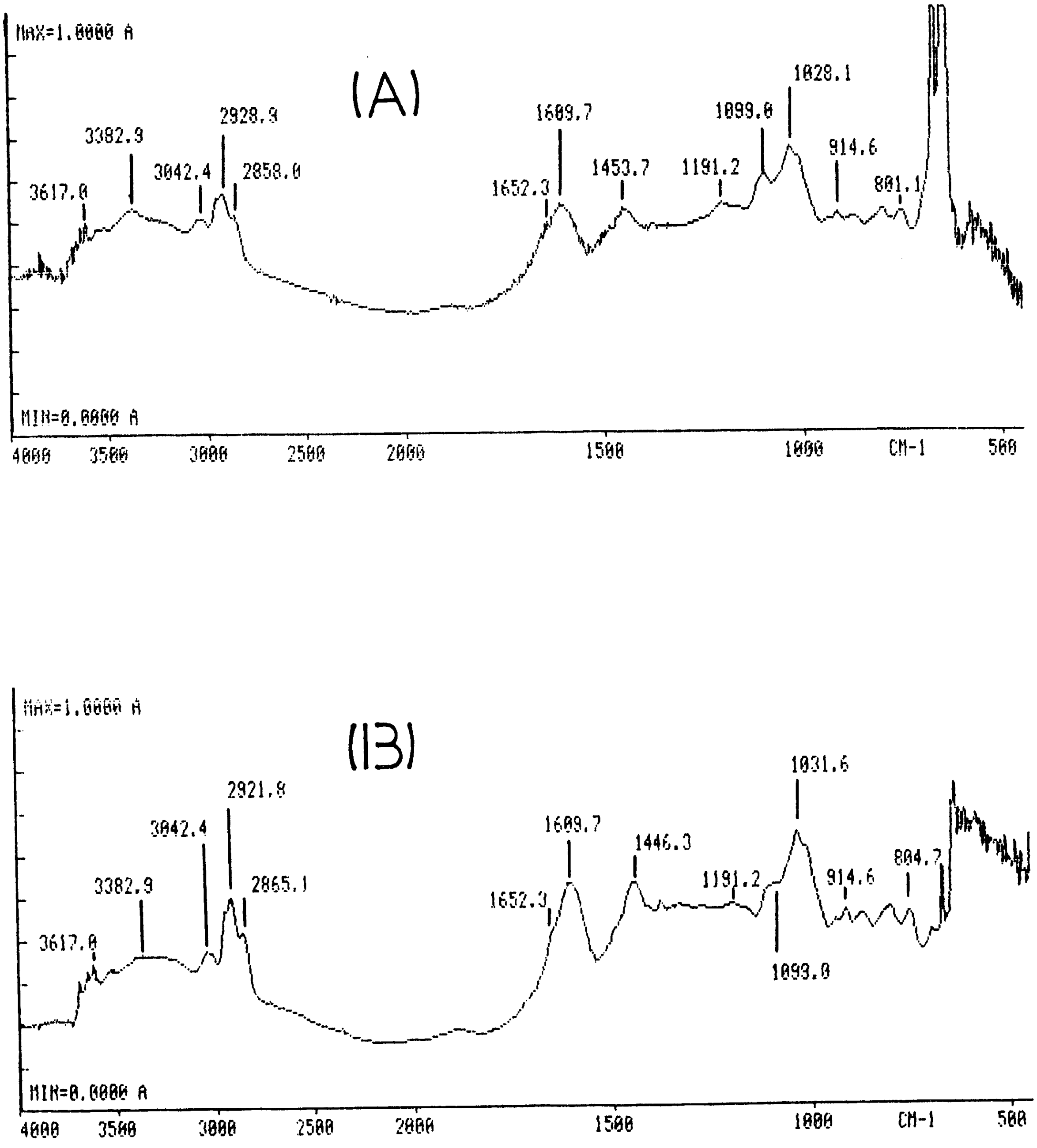

Figure 4: DRIFT spectra of MV bituminous C (PSOC-1527) coal; (A): as-received; (B): oxidized with 1.0 M HNO_3 for 5 hours at room temperature

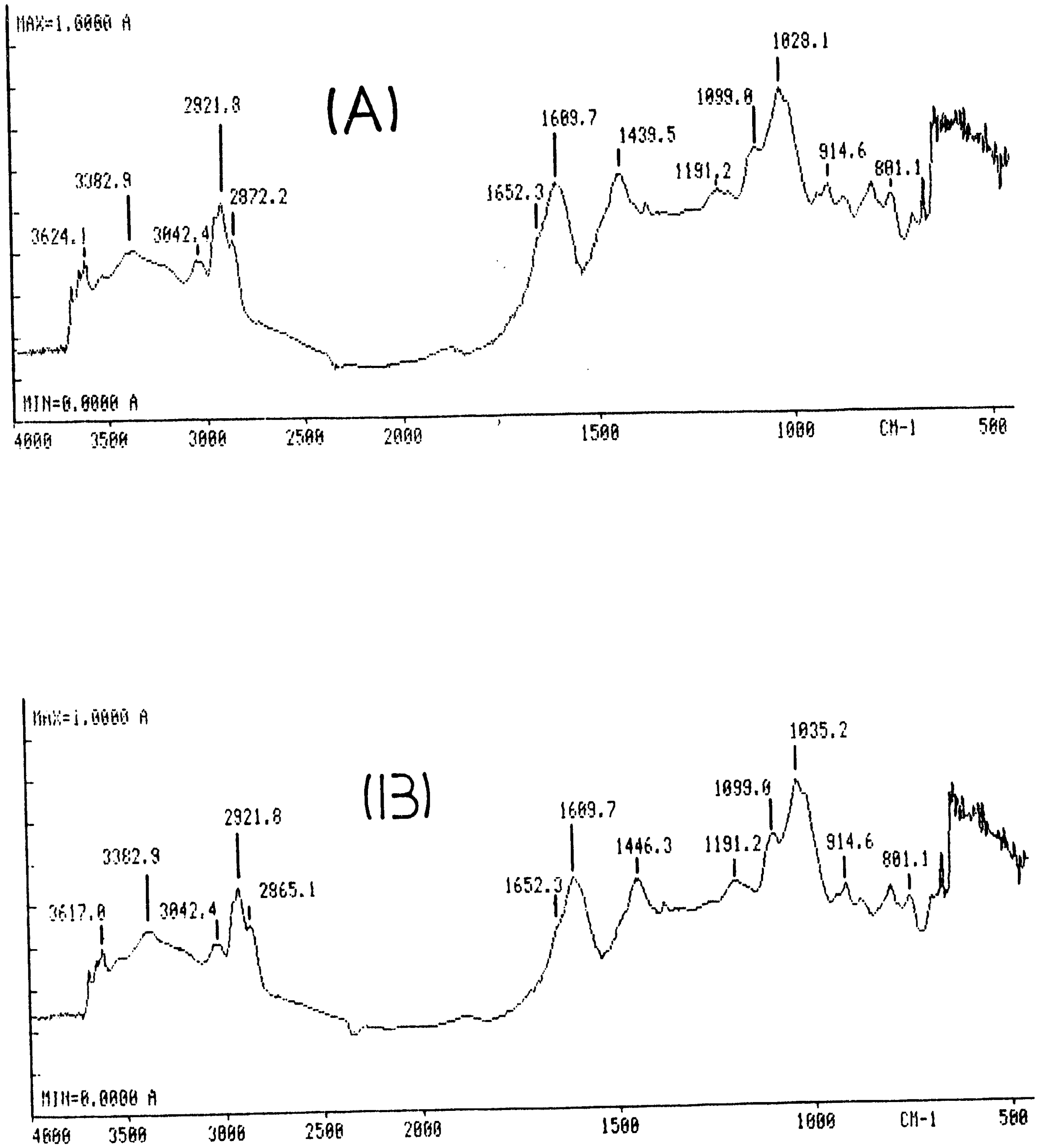

Figure 5: DRIFT spectra of MV bituminous C (PSOC-1527) coal; (A): oxidized with H_2O_2; (B):oxidized with 0.05 M $Fe_2(SO_4)_3$ for 5 hours at room temperature

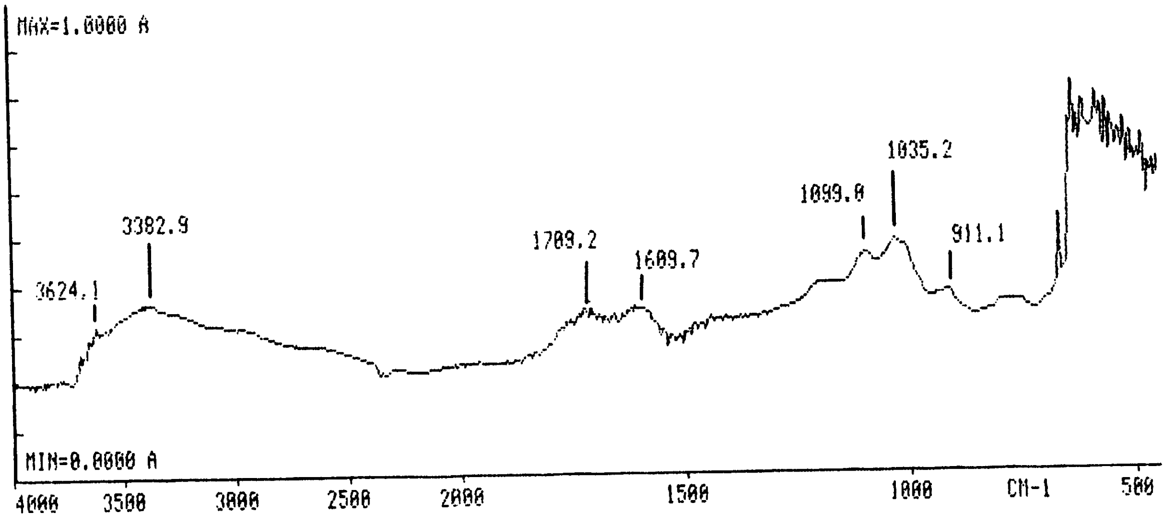

Figure 6: DRIFT spectrum of MV bituminous C (PSOC-1527) coal oxidized with air at 230° C for 24 hours

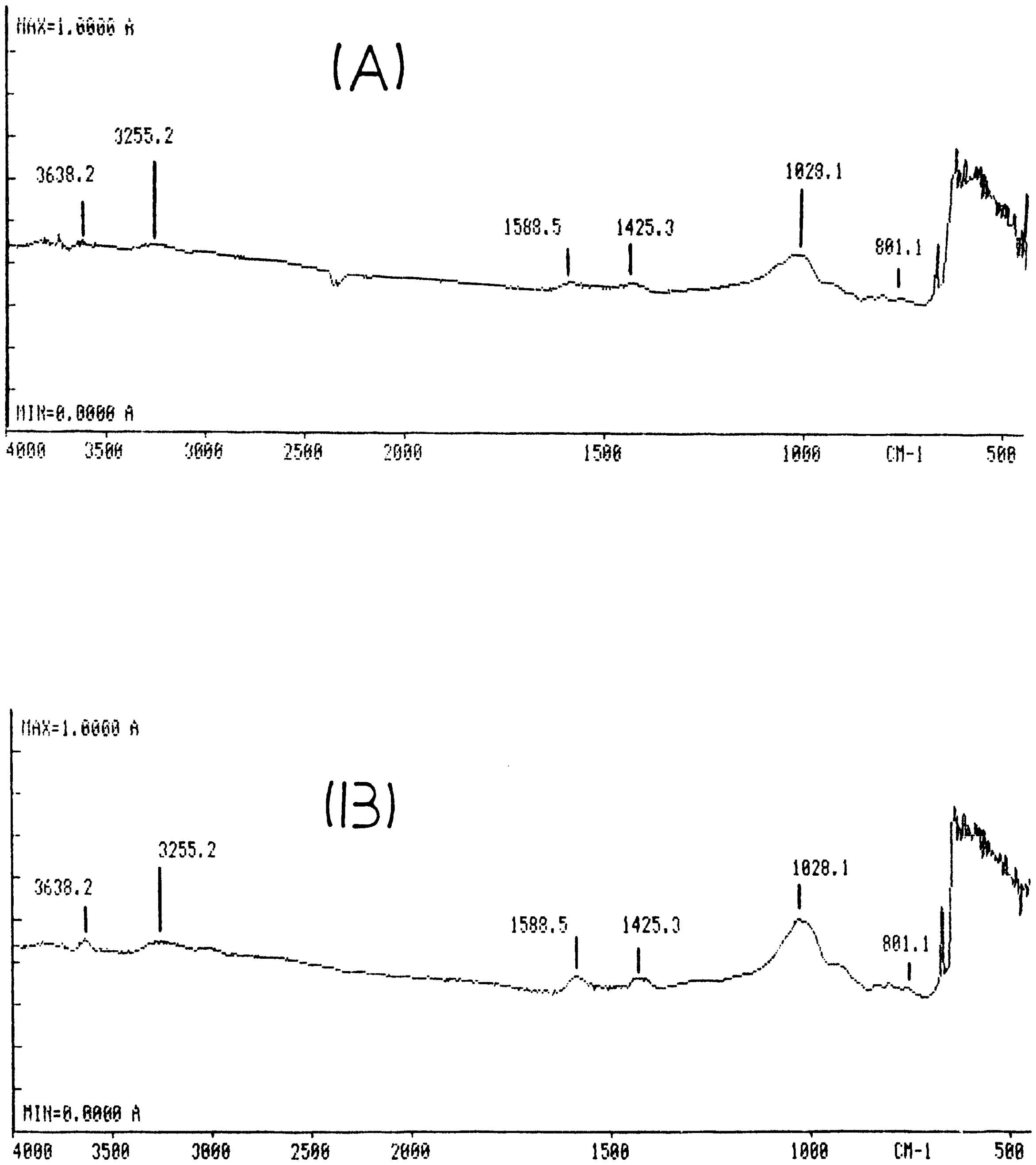

Figure 7: DRIFT spectra of anthracite (PSOC-1461) coal; (A): as-received; (B): oxidized with 1.0 M HNO_3 for 5 hours at room temperature

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