Nitrogen Chemistry of Kerogens and Bitumens from X-ray Absorption Near-Edge Structure Spectroscopy

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X-ray absorption near-edge structure (XANES) spectroscopy studies have been conducted on several different kerogens and bitumens to identify all the different nitrogen chemical structures present. Virtually all of the nitrogen is present in aromatic forms; pyrroles are the most dominant type, followed by pyridines, pyridones, and aromatic amines. A considerable amount of porphyrinic nitrogen, characterized by significant spectral effects, is found in one of the bitumens. The pyridone fraction in the kerogens and bitumens is much larger than in petroleum asphaltenes, suggesting that petroleum generation is accompanied by the loss of pyridone, possibly by conversion to pyridines. Differences are found between the kerogens and bitumens from the same source rock, indicating that bitumen analysis cannot substitute for kerogen analysis at least for nitrogen chemistry. There is no qualitative difference in the types of nitrogen compounds between kerogens produced by HCl or HF digestion.

Introduction

Kerogens and bitumens are important, organic entities of sedimentary rocks; the maturation of kerogens and bitumens over geological time results in the production of crude oil. The intricacies of the maturation process are, however, not well understood. Heteroatoms, such as nitrogen, present in the kerogens and bitumens can be used as probes for understanding maturation of these materials. Elucidation of the complex chemistry of heteroatoms can reveal subtleties about the maturation process. In a more general sense the chemistry of heteroatoms in fossil fuels and their heavy ends is of interest. The presence of sulfur and nitrogen hinders the use of fossil fuels due to both the increased difficulties of processing and the increased environmental hazard of waste products. It is also instructive to compare the heteroatom chemistry of kerogens and bitumens with asphaltenes and other fossil fuels such as coals to monitor the maturation process. Many studies have been conducted to elucidate the nitrogen chemistry of these organic entities in kerogens; however, often these studies are destructive or insensitive to substantial fractions of nitrogen. In contrast, X-ray absorption near-edge structure (XANES) studies are both direct and nondestructive; all nitrogen in the sample provides a XANES signal. Here, we report the results of the first nitrogen XANES studies performed on several immature kerogens and bitumens.

Kerogen is the solid, insoluble organic fraction of source rocks. Kerogen from Green River oil shales is one of the most studied kerogens, and is classified as a type I kerogen. The H/C ratio in an immature Green River kerogen is typically 1.5, and the O/C ratio is less than 0.1.[1] There are a large number of aliphatic chains in type I kerogens. Polycyclic aromatic hydrocarbons and heteroatom-containing compounds are present in relatively small amounts.[2] Bitumen is the dark brown, viscous, solvent-extractable organic part of shales and source rocks of crude oils. The bitumen content of an oil shale is typically 5% of the total organic matter.[3] The H/C ratio is roughly 1.5 in type I bitumens as in kerogen, and the number-average molecular weights are typically around 1200.[3]

Type I kerogens and bitumens originate largely from unicellular organisms which contain large amounts of lipids, which are deposited in reducing environments. The maturation process of kerogens is similar to that of coal in that the combined action of heat and pressure in the presence of water and inorganic materials results in significant modification of the source materials. Kerogen maturation over geological time (diagenesis) may result in the production of crude oil, as well as more mature kerogen. Coals, on the other hand, originate from higher forms of plant life which contain woody materials and resins, and the depositional environment of coal is more oxidizing, particularly initially, than the kerogen environment.

Earlier studies on the nitrogen structures present in kerogens have been limited by their insolubility; IR, NMR, and MS analyses of reagent-treated kerogens have revealed that quinoline, indole, and pyridine derivatives are often present in Green River kerogen.[4] Bitumens from Green River oil shales have been analyzed using GC–MS, and evidence of quinolines, tetrahydroquinolines, and, to a lesser extent, pyridines and indoles has been found.[5] LC

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and GC–MS studies have shown that some bitumens also possess nitrogen-containing aromatics such as azarenes, azadibenzothiophenes, and also cyclic amides.[6] However, distributions of nitrogen compound types in bitumens do not necessarily give kerogen distributions.

X-ray absorption near-edge structure (XANES) spectroscopy is an excellent nondestructive and direct method for determining different heteroatomic structures present in complex systems such as fossil fuels. Sulfur XANES studies have been successfully conducted on fossil-fuel samples, such as coal[7-12] and petroleum asphaltenes,[13,14] for the past 10 years in order to determine constituent sulfur structures. XANES studies have shown that coals and petroleum asphaltenes have both saturated and aromatic forms of sulfur; thiophene (aromatic) is the most dominant sulfur form followed by the sulfidic (saturated) form. Oxidized forms of sulfur are often found in smaller quantities in coals and asphaltenes; organic sulfoxide and sulfone and inorganic sulfate are the common oxidized sulfur forms found in coals, and petroleum asphaltenes contain small amounts of sulfoxide. Pyritic sulfur is often found in coals.

Nitrogen XANES studies performed on coals,[15,16] and petroleum asphaltenes,[15,17] have also been very successful in determining nitrogen compound type distributions. It is found that nitrogen structures are primarily aromatic in the fossil-fuel samples, with little or negligible quantities of saturated nitrogen compounds. Pyrrolic and pyridinic compounds of nitrogen are the most common nitrogen-containing constituents in fossil fuels, and the coals also contain substantial amounts of pyridones and aromatic amines. Low-rank coals, which have high oxygen content, have a much greater quantity of pyridone analogues and a smaller quantity of pyridine than the higher rank coals; this implies that the process of maturation of coals eliminates oxygen from pyridone, forming pyridine. The amount of aromatic amines in coals is small, but significant. Petroleum asphaltenes, on the other hand, do not show the presence of significant amounts of pyridones or aromatic amines. (In this paper, we will refer to pyridines, pyridones, and pyrroles as representing classes of compounds with the same functional group, as opposed to a particular compound.)

This paper presents nitrogen XANES results of three oil shale bitumens, one kerogen sample, and two debitumenized, decarbonated oil shales. (The latter two samples were subjected to only relatively mild conditions to concentrate the kerogen.) These are the first nitrogen XANES studies performed on such samples. All the features of the XANES spectra of kerogens and bitumens have been described, and therefore all the nitrogen chemical structures present in these samples have been accounted for. The XANES spectra of several different types of nitrogen model compounds have been studied; they are pyridine, pyridone, pyrrole, aromatic amine, porphyrin, and saturated amine. The XANES spectrum of each different nitrogen structure exhibits the major lowest energy resonance (π^* resonance for aromatic molecules, and σ^* for saturated molecules) at a characteristic energy. XANES spectra of the kerogens and the bitumens have resonances which match in energies with those of the different characteristic resonances of the model spectra; thus, the presence of the different molecules in these fossil-fuel materials can be identified readily.

Experimental Setup

XANES data on all the kerogen and bitumen samples were obtained at the soft X-ray beam line U4B, constructed by AT&T Bell Labs,[18] at the National Synchrotron Light Source at Brookhaven National Laboratory. A grating monochromator was used for the experiment, with a grating of 600 lines/mm. Pressures of 10^{-9} to 10^{-10} Torr were maintained in the sample chamber by means of a turbo molecular pump and a cryopump. The samples were mounted on nitrogen-free 3M tape on the holder and positioned in the sample chamber by means of a load-lock system. Both a multielement germanium detector[19] and an electron channeltron detector were used to obtain data in the fluorescence and electron-yield modes, respectively. The Ge detector signal was amplified using a 2-μs shaping time, and the total count rates were about 1500 counts/channel. The channeltron voltage was typically around 1000–1500 V. The energy resolution employed was around 140 meV at 400 eV.

The fossil-fuel samples consisted of three bitumens, a kerogen, and two debitumenized, decarbonated shales (which we will also refer to as kerogens in this paper because, by definition, any organic nitrogen compound is a kerogen component). The two debitumenized, decarbonated shales (GRK-1, GRK-2) and the corresponding bitumens (GRB-1 and GRB-2) were obtained from Green River oil shales. The third kerogen sample was also obtained from Green River oil shales. Green River oil shales are marls, and they contain appreciable amounts of carbonate. Two of the bitumens were extracted from Green River oil shales, and the third bitumen was extracted from New Albany (NAB) shale. All the shales were first pulverized, and then they were extracted in a Soxhlet extractor using a benzene methanol mixture which was then filtered and dried. The kerogens were concentrated by the relatively mild process of HCl digestion of the carbonate. After treating the kerogens with HCl twice, the samples were heated and stirred, filtered, washed with water, and dried. HCl digestion does not remove the silaceous materials from the kerogen, unlike HF digestion. The third kerogen (G-3) was demineralized using HF, and has been stored in normal atmospheric conditions for many years. The kerogens examined here are of low maturity and are type I. Both the kerogens and bitumens are nonvolatile, and are dark brown to black in color; the kerogens are powdery, while the bitumens are similar in appearance to a heavy tar. These samples were obtained from Western Research Institute, Laramie, WY.

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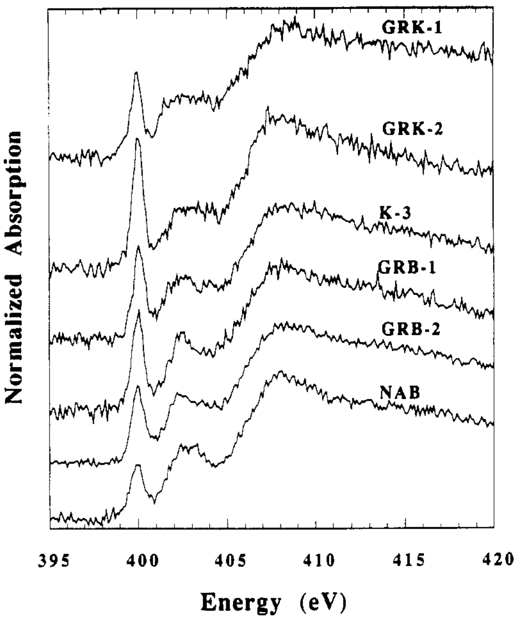

Figure 1. Fluorescence XANES spectra of three kerogens, GRK-1, GRK-2, and K-3, and three bitumens, GRB-1, GRB-2, and NAB. Analysis of the resonances structures in the spectra allows identification of constituent nitrogen chemical structures.

HCl treatment of two of the marl samples removed carbonates from the mineral matrix of the shales. Silicates and some other minerals remain along with the kerogen. The decarbonation procedure serves to concentrate the organic compounds (with nitrogen) in the samples studied. Using only the mild conditions required for decarbonation makes unlikely any alteration of the organic material.

The nitrogen model compounds consisted of five pyridine analogues, acridine, poly(4-vinylpyridine-*co*-styrene), phenanthridine, 4,7-phenanthroline, and 2,6-di-*p*-tolylpyridine; four pyridone analogues, 6-(2,2-diphenyl-2-hydroxyethyl)-2(1*H*)-pyridone, 2-hydroxypyridone, 1-hydroxyisoquinoline, 1-methyl-4-pentadecyl-2(1*H*)-quinoline; four pyrrole analogues, carbazole, tetrahydrocarbazole, poly(9-vinylcarbazole), and 2-phenylindole; two aromatic amines, 5-aminofluorene and aminochrysene; two porphyrin compounds, (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine)nickel(II), and (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine)vanadium(IV) oxide; and two saturated amines, 1-3-5-tribenzylhexahydro-1-3-5-triazine and 1,12-diaminododecane. All the model compounds were obtained from Aldrich Chemical Co., and were used without further purification.

Results and Discussion

Figure 1 shows nitrogen XANES spectra of three kerogens and three bitumens; all the spectra in Figure 1 are normalized with respect to the corresponding step heights. All the XANES spectra show three distinct resonance features. The first resonance region is a rather sharp feature occurring at roughly 400 eV, the second region at $\sim$403 eV is very broad, and the third resonance region is more intense and broad, and occurs at $\sim$408 eV. Some variability in peak amplitudes is observed. All three kerogen spectra have a small valley at $\sim$404.5 eV; this valley is deeper in the bitumen spectra. There is no large difference observed between the spectra of the hydrofluoric acid-treated kerogen and the two hydrochloric acid-treated kerogens. The feature at $\sim$402.6 eV in the bitumen spectra appears to be slightly shifted and more intense than the second resonance seen in the kerogen spectra.

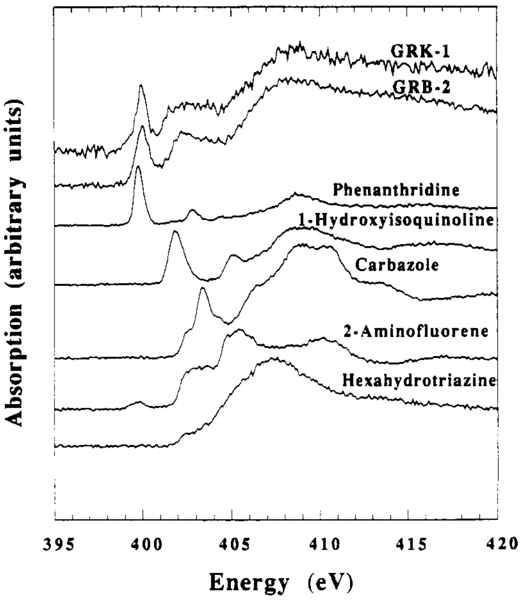

Figure 2. Fluorescence XANES spectra of a kerogen, a bitumen, and analogues of each of five different nitrogen structures: pyridine, pyridone, pyrrole, aromatic amine, and saturated amine. All the spectra are normalized with respect to the corresponding step heights. The first resonance energy of the kerogen and bitumen spectra match well with the pyridine π^* energy, indicating the presence of pyridine structures in the fossil-fuel samples. Likewise, the correspondence between different resonance energies of the kerogen and bitumen spectra with the major π^* resonances of the model spectra indicate the presence of these different nitrogen chemical structures in the fossil-fuel spectra.

Figure 2 shows the XANES spectra of a kerogen (GRK-1), a bitumen (GRB-2), and an analogue each of pyridine, pyridone, pyrrole, aromatic amine, and saturated amine. The first resonance energy of both the kerogen and the bitumen spectra match well with the π^* resonance of the pyridinic analogue phenanthridine. The lower energy feature of the second region, at $\sim$402 eV, especially in the kerogen spectrum matches well with the π^* resonance of the pyridone analogue 1-hydroxyisoquinoline. The 403-eV feature in the spectra of both the kerogen and the bitumen match well with the π^* resonances of the pyrrole analogue carbazole, and the 405-eV feature in the kerogen and bitumen spectra can be attributed in part to aromatic amine structures, as the XANES spectra of the aromatic amines have broad resonances at this region. The matching energies between the fossil-fuel and the model spectra imply the presence of the respective nitrogen structures in the fossil-fuel spectra, and the presence of different nitrogen structures in the fossil-fuel samples can be determined. Variation in amplitudes of the different resonances in these fossil-fuel samples shows variability in the quantities of different nitrogen structures present.

The quantification of pyridine structures is the most apparent because the pyridine peak is isolated and readily identified. The lowest energy resonance of the pyridone analogues is always at a lower energy than the lowest energy resonance of the pyrrole analogues, thereby allowing the quantitative determination of these two chemical structures. However, because the resonance regions of pyridones and pyrroles are close and not clearly separated, some uncertainty exists in this quantitative determination. The absorption of the aromatic amines overlaps with the spectral valley of the pyrroles. However, the pyrroles do have significant absorption in this spectral valley. Absorption in this spectral region above that of pyrrole analogues is assigned to aromatic amines. This method gives an approximate quantity of aromatic amines present.

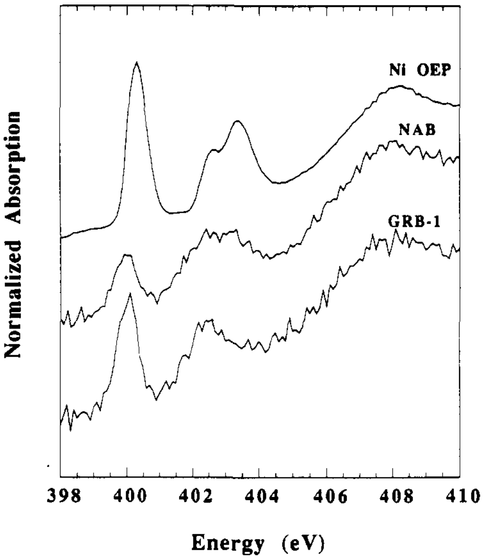

Figure 3. XANES spectra of two bitumens, GRB-1 and NAB, and Ni OEP. The NAB spectrum has a peak at ~403.4 eV, while the GRB-1 spectrum does not. This same peak is present in the porphyrin spectrum. This, coupled with the fact that NAB sample is high in V and Ni content, indicates the presence of considerable amounts of porphyrin in the NAB sample.

The quantity of aromatic amines is always found to be rather small; thus, the absolute error is limited.

Earlier studies[16,17] have shown that the characteristic π^* resonances of analogues of a particular kind of nitrogen chemical structure occur at similar energies (usually within 0.9 eV) and, for some nitrogen structures, are well-separated from those of analogues belonging to a different kind of structure ($\Delta E \approx 1.5$ eV). This has been explained[16,17] in terms of the behavior of the lone pair of electrons at the nitrogen site; the more negative nitrogen site in the pyridine molecules exhibits red-shifted π^* resonances compared to the more positive nitrogen site in the pyridone and pyrrole molecules.

The pyridone compounds can exist in two tautomeric forms, the keto (or amide) form and the enol form. The enol is clearly aromatic as is the keto form at least to an extent due to the lone pair of electrons of the nitrogen in the p_z orbital. IR spectroscopic studies have shown that pyridone does exist to some extent in the keto form.[20] Our analysis is independent of which tautomer exists in the model compounds and fossil fuels. All of the pyridone analogues which we have investigated produce a large π^* resonance at nearly the same energy. Thus, if the equilibrium is varying from one compound to another, it is not readily apparent in our data.[16,17] Furthermore, in the determination of the pyridone analogue content in the kerogens and bitumens, we are not concerned with the tautomeric equilibrium. We make the assumption that our pyridone model compounds, whatever their tautomer form and hydrogen bonding, represent good models for the same chemical function in the fossil-fuel samples.

Figure 3 shows the XANES spectra of nickel octaethylporphyrin, NAB bitumen, and GRB-1 bitumen. The first peak in all three spectra match in energy (~400 eV). The second resonance region in the NAB spectrum is similar to that of the GRB-1 spectrum, except that in the spectrum of NAB there is an enhanced peak at 403.4 eV, which is absent in the spectrum of GRB-1. This 403.4-eV peak is also present in the porphyrin spectrum. Furthermore, NAB contains large amounts of V and Ni (analysis performed by Galbraith Laboratories). There is a significant porphyrin fraction present in the NAB sample which is determined by the presence of a large Soret band in the optical absorption spectrum of this sample. Previously we have discussed[17] that porphyrins have both pyridinic and pyrrolic types of nitrogen in the molecule. The two porphyrin nitrogen atoms with a formal double bond are (defined to be) pyridinic, with the nitrogen lone pair of electrons in an sp^2 orbital. The two porphyrin nitrogen atoms which are formally charged in metalloporphyrins, or bonded to hydrogen in free base porphyrins, are pyrrolic, with the lone pair occupying the p_z orbital. The 400-eV peak in the porphyrin spectrum is due to the presence of pyridinic-type nitrogen present in the porphyrin molecule,[17] and the second resonance region in the porphyrin spectrum is likewise due to the presence of pyrrolic nitrogen in the molecule.[17] The pyrrolic nitrogen peak of porphyrin is slightly shifted from that of other pyrroles, producing a recognizable porphyrin feature in NAB.

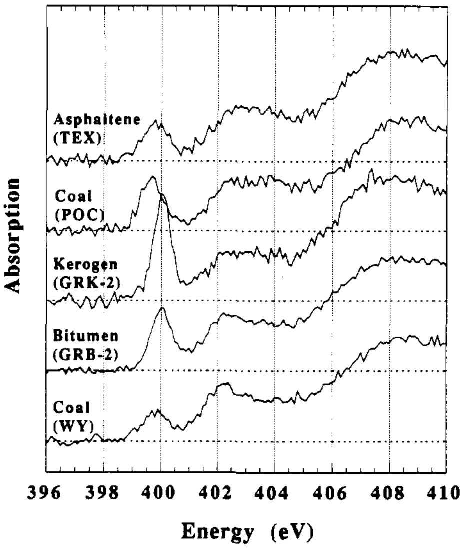

Figure 4. Fluorescence XANES spectra of several fossil-fuel samples, shown on an expanded energy scale: a petroleum asphaltene, TEX, high-rank coal, POC, a kerogen, a bitumen, and a low-rank coal, WY. All the spectra are normalized with respect to corresponding step heights. The characteristic pyridone resonance absorption at ~402 eV in the spectra of the petroleum asphaltene and the high-rank coal is hardly discernible, but it is relatively more intense in the spectra of the other fossil-fuel samples. During the process of maturation from a low-rank to a high-rank coal, the pyridone structures in coal transform into other forms; a similar situation prevails as immature kerogens and bitumens are converted into crude oil.

Pyridone appears in low-maturity samples, but not high-maturity samples. In Figure 4 we show directly the spectral effect of pyridone on fossil-fuel spectra. The spectra of a kerogen, a bitumen, a high-rank coal (POC), a low rank coal (WY), and an asphaltene (TEX) are shown in Figure 4. The feature at 402 eV, which is a signature of the presence of pyridone, is increasingly more enhanced in the spectra of samples in the following order: asphaltene, high-rank coal, kerogen and bitumen (both have comparable intensities), and low-rank coal. This feature in the spectra of the asphaltene and the high-rank coal is rather small, indicating the presence of very small, if any, quantities of pyridone in these samples; the same feature is much more prominent in the kerogen, bitumen, and a

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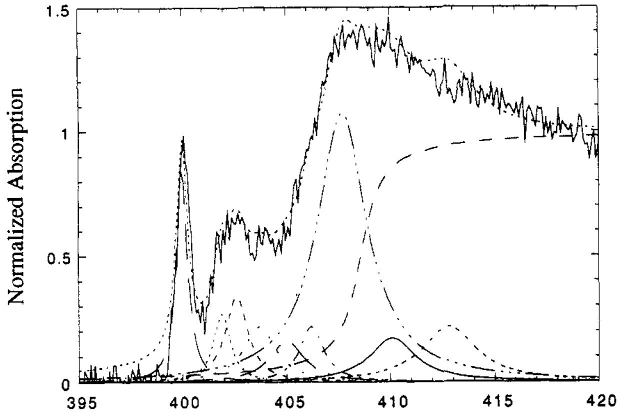

Figure 5. Results of fitting the K-3 kerogen spectrum with the different peaks used to determine nitrogen fractions as described in the text. The resultant sum matches the data quite well.

low-rank coal (high oxygen content). This leads to the argument that mature samples, such as high-rank coals and asphaltenes, have only small amounts of pyridone in contrast to the immature shales and low-rank coals, and is in accord with the known reduction of oxygen content with maturation.

Least-squares fitting routines were employed to evaluate the normalized peak areas of the different features in both the fossil-fuel and the model spectra. All the spectra were normalized with respect to the step height, and the spectra of all the analogues of a particular nitrogen type were then summed up. The resulting spectral sum was then fit with nine Lorentzian resonances and one arc-tangent step. The parameters of these resonances were: 400 eV, $\Delta\nu = 0.65$ eV (pyridine), 401.9 eV, $\Delta\nu = 0.97$ eV (pyridone), 402.6 eV, $\Delta\nu = 1.3$ eV, and 403.7 eV, $\Delta\nu = 1.9$ eV (pyrrole), 405.0 eV, $\Delta\nu = 2.0$ eV (aromatic amine), 406.2 eV, $\Delta\nu = 1.4$ eV, and 407.7 eV, $\Delta\nu = 2.9$ eV (all models including saturated amines), and 410.1 eV, $\Delta\nu = 2.7$ eV, and 412.8 eV, $\Delta\nu = 3.2$ eV (continuum resonances). The arc-tangent step had a width of 1.5 eV, and was positioned at 408.6 eV. Corresponding normalized areas for each analogue were then calculated. Figure 5 shows the result of fitting a kerogen (K-3) with the peaks listed above; the resultant sum of the fitted peaks closely matches the data. Similar fits are obtained with the model compounds.

Even though there is some overlap of the sides of the pyridone and pyrrole absorption, the absorption peaks of pyridones and pyrroles are definitely resolvable. The lowest energy resonances of the pyridone models we have run are in the range of 401.6–402.1 eV, while those for the pyrroles are in the range 402.5–404 eV. With fossil-fuel samples, the ranges may be larger, but the resolvability of pyrrole and pyridone is substantial.

Table I. Normalized Areas Obtained by a Least-Squares Fit of the Sum of Spectra of Analogues of Particular Nitrogen Types at Particular Energies

summed spectrum	399.7 eV (pyridine)	401.9 eV (pyridone)	402.6, 403.7 eV (pyrrole)	405 eV (ar amine)	406.2, 407.7 eV (satd amine)
porphyrin	1.47		1.53		5.07
pyridine	3.56		0.98	0.54	4.40
pyridone		2.01		0.40	6.03
pyrrole			2.49		6.39
ar amine			1.82	2.87	5.31
satd amine			0.44	1.94	10.94

Table I lists the normalized area values obtained as a result of the least-squares fit of the spectra of the sum of analogues of each nitrogen structure. Pyridine and pyridone do not have any overlapping areas at the principal π^* resonance energies, nor do pyridone and pyrrole. Also, as explained earlier, half of the nitrogen in porphyrins is pyridinic and half pyrrolic. The second step of the analysis procedure was to fit the kerogens and the bitumens with the same number of resonances and the step function having the same parameters as used for the model spectra. The first resonance area was attributed to pyridine, the second to pyridone, the third and fourth to pyrroles, and the fifth to aromatic amines. The sixth and seventh resonances were attributed to saturated amines. The relative percentages of the different nitrogen structures were then calculated. When determining the percentage of a particular model structure, care was taken to subtract from the fossil-fuel spectrum any contribution at that energy arising from other model spectra. For instance, the summation spectrum of the pyridine structure has a small contribution in the pyrrole region; therefore, this fraction was subtracted when calculating the pyrrole fraction.

Table II summarizes the relative percentages of the different nitrogen structures present in the kerogen and the bitumen samples. In our analysis procedure, the peak area percentages are normalized by the peak amplitudes for the different nitrogen structures, thereby resulting in percentages of the different nitrogen chemical structures. Significant variation is observed in the percentages of the different nitrogen fractions present in these fossil-fuel samples. Most of the nitrogen is present in aromatic forms, with zero or small amounts of saturated fractions. Pyrrole is the most dominant nitrogen structure in the kerogens and bitumens, as its fraction ranges between 42% and 67% of the total nitrogen content. Pyridone fractions vary from 11% to 23% of total nitrogen. The aromatic amine fractions are generally small, ranging from 8% to 15%. The saturated amine fractions are mostly zero, except in kerogen GRK-2, which contains about 11% saturated amine. Of all the kerogens and bitumens, and from earlier studies, coals and asphaltenes, this is the only sample which contains saturated amine and only at the level of our error. Thus, the level of saturated amine in this sample may be overestimated. We estimate the error in the entries in Table II to be approximately 10%. No fundamental difference between kerogen and bitumen is found, indicating acid treatment of the kerogens, but not the bitumens, produces no observable effects.

In the NAB sample, least-squares analyses were performed once by the above method, and a second time using porphyrin as an extra nitrogen model in addition to the other models. The porphyrin percentage was first estimated from the V and Ni content. We assumed that all of the vanadium and nickel present in the sample was complexed in prophyrin structures in the NAB sample. By knowing the nitrogen mass fraction, we could then determine the fraction of nitrogen which exists in porphyrins. This percentage of porphyrinic spectral contribution was subtracted from the NAB spectrum before determining percentages of other nitrogen structures. Both the results (with and without porphyrin explicitly included) are also given in Table II. Twenty-one percent of the nitrogen in the NAB sample is porphyrinic. As expected, half of the porphyrin percentage is due to pyridinic nitrogen and the other half to pyrrolic nitrogen; our results show that the pyridinic and pyrrolic results in the two

Table II. Percentages of Different Nitrogen Structures Present in the Kerogens and Bitumens

sample	% pyridine	% pyridone	% pyrrole	% ar amine	% satd amine	% N[b]
kerogen GRK-1	20	23	42	15	0	1.09
bitumen GRB-1	27	11	49	11	2	0.83
kerogen GRK-2	34	11	42	2	11	1.03
bitumen GRB-2	20	19	49	12	0	1.47
kerogen K-3	24	20	45	10	0	1.81
bitumen NAB	14	11	67	8	0	2.60
bitumen NAB (21% porphyrin)[a]	6	11	55	9	0	2.60

[a] Only sample with appreciable porphyrin. The porphyrin percentage is estimated from the V and Ni content in the butumen. The porphyrin contribution was subtracted from the peak areas, and the standard analysis was employed on the remaining 80% nitrogen. [b] Analysis performed by Galbraith Laboratories, Knoxville, TN.

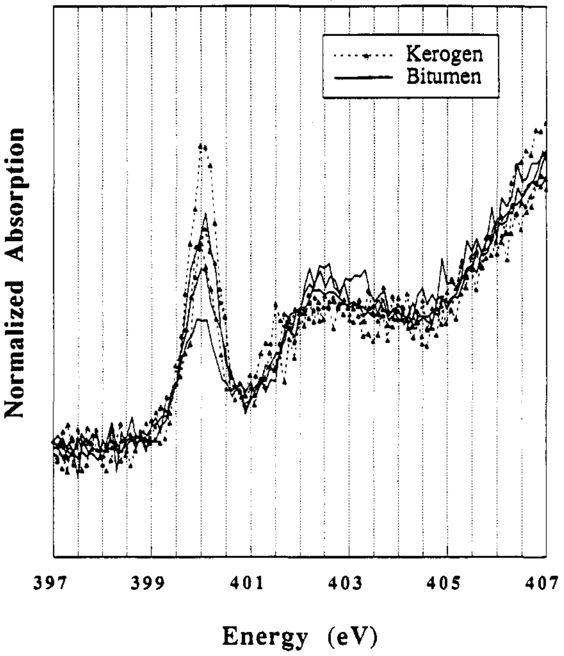

Figure 6. An overlay of the fluorescent spectra of the three kerogen and the three bitumen spectra. The bitumen spectra have more intense peaks at ~402.5 eV than the kerogen spectra. This region falls in between the pyridone and pyrrole regions, and could arise from structures close to those of pyridones or pyrroles. The pyridine peak intensity at ~400 eV is less intense in the bitumen spectra in general than in the kerogen spectra. The rising slope at ~406 eV in the two sets of spectra overlay each other very closely.

cases differ from each other by ~10% which is just the porphyrin contribution to the two nitrogen types. The pyridone and aromatic amine contents for the two analyses remain essentially the same.

Figure 6 shows an overlay of the three kerogen and the three bitumen spectra; the dashed lines belong to the kerogen spectra, and the solid lines to the bitumen spectra. Both sets of kerogen and bitumen data show the presence of the same constituent nitrogen structures: pyridine, pyridone, pyrrole, and aromatic amine. Figure 1 shows that the bitumen spectra have enhanced peaks at 402.5 eV unlike the spectra of kerogen. This 402.5-eV resonance falls in between the pyridone and pyrrole regions (Figure 2); this peak in the bitumen spectra could arise from the presence of other pyridone analogues, or from other forms of nitrogen with structures similar to those of pyrroles.

This new analysis procedure was also employed to investigate the nitrogen forms present in the entire suite of Argonne coals[17] and in petroleum asphaltenes,[16] which have been studied before. The new results obtained match very well with the prior results, within a deviation of only a few percent. The new results of petroleum asphaltenes show low concentrations of pyridones (<6%) and aromatic amines (<4%), whereas the coals show larger amounts of both these structures. Low-rank coals are high in pyridone and low in pyridine content, in contrast to the high-rank coals.

Table III. Energies, Standard Deviations of Energies, and the Widths of the Characteristic Pyridine Resonances of the Different Samples

	energy (eV)	std dev (eV)	width (eV)
pyridine models	399.73	0.29	0.6–0.9
kerogens and bitumens	400	0.06	0.6–0.8
coals	399.8	0.08	0.6–1.0
petroleum asphaltenes	399.7	0.09	0.7–1.0

Table III lists the average, the standard deviation, and the range of widths of the π^* energies of several pyridine analogues, kerogens, bitumens, coals, and petroleum asphaltenes. The pyridine analogues used for this table consist of varied numbers of fused rings. The energy of the first resonance in the spectra of the petroleum asphaltene and coal, both of which are mature fossil-fuel samples, is slightly red shifted when compared to the same feature in the spectra of the kerogen, bitumen, and to some extent, low-rank coal. Our earlier work[16] has shown that there is a slight tendency with pyridine structures containing more than one ring systems to have their π^* resonances at somewhat lower energies than structures containing only one ring system. This suggests that pyridine structures with smaller rings tend to dominate in the less mature samples, such as type I shales, and that those containing more than one ring tend to be more abundant in the more mature samples, such as high-rank coals and petroleum asphaltenes.

The energies of the first resonances of the fossil-fuel samples occur well within the energy span covered by the π^* resonances of the different pyridine models.[16,17] Also, the standard deviations of peak positions in the XANES spectra of the fossil-fuel samples are smaller than the energy range spanned by the characteristic π^* resonances of the different pyridine analogues. This suggests, surprisingly, that the fossil-fuel samples might not contain a large distribution of pyridine structures; the small peak width might be due in part to the nonuniformity of the peak intensities relative to the step height for the different pyridine analogues.

Conclusions

Nitrogen XANES studies have been successful in detecting and quantifying the different nitrogen structures present in complex kerogen and bitumen samples. Several nitrogen model compounds have been studied in order to determine the nitrogen structures present in these oil shale components. Nitrogen is present primarily in aromatic structures, with pyrrolic nitrogen being the most dominant type. Significant pyridinic nitrogen is also found. Bitumen NAB contains a significant amount of porphyrin fraction which produces an evident spectral effect. Pyridone was detected in kerogens and bitumens, but not in asphaltenes, suggesting that maturation results in the conversion of pyridone into pyridine. This conversion was convincingly established previously in the maturation of low-rank coals. Small quantities of aromatic amine are also present in both these types of samples. The kerogen and bitumen from the same source rock differ in their nitrogen percentages, so the bitumens, which are more easily isolated, cannot be used as a substitute for kerogen for analysis purposes. No significant trends are observed among the kerogens and bitumens from the same source rock. The percentages of the different nitrogen structures found in the HF-treated kerogen does not differ much from those in the HCl-treated kerogens. Kerogens and bitumens are not fundamentally different with respect to nitrogen, so acid treatment of the kerogens does not produce observable effects here. The first resonances in the spectra of kerogens and bitumens, which are relatively immature compared to coals and petroleum asphaltenes, are found at higher energies than the latter samples. This may be due to the presence of larger aromatized structures in the more mature samples than in these kerogens and bitumens. There is some uncertainty regarding the origin of the peak at 402.6 eV in the spectra of bitumens, and this feature may correspond to oxidized pyrroles. In conclusion, XANES has once again proved to be a valuable analytical tool for determining different nitrogen structures present in complex, heterogeneous materials such as kerogens and bitumens.

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