

Aromatic And Aliphatic Carbon Contents
of Coals and Oil Shales by ^{13}C NMR

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For many types of samples in the field of fossil fuels, e.g., oil shales and typical coals, only a small fraction of the organic substances can be extracted from a solid under mild conditions that would be expected to retain the primary structural integrity of the organic compounds. Hence, the constraint of analytical techniques to liquid samples has been very restrictive. This constraint has been shared by nuclear magnetic resonance (nmr), for which high-resolution analytical applications have been limited to liquid samples until very recently. The "standard" ^{13}C nmr techniques, including pulse Fourier transform (FT) approaches¹ have not been generally useful for solid samples because of (a) the excessive line broadening due to dipole-dipole interactions between ^{13}C and ^1H magnetic dipoles, (b) chemical shift anisotropies (different shielding values for the many different orientations of the molecules in an amorphous state with respect to the magnetic field direction), and (c) long ^{13}C spin-lattice relaxation times (T_1).² All of these problems are eliminated in liquids (or in the case of long T_1 values, at least greatly reduced) by the normal tumbling motions occurring randomly in the liquid state.

This paper is concerned with the refinement and application of recently introduced ^{13}C nmr techniques for obtaining high resolution spectra of solid samples. Dipolar line broadening in the ^{13}C spectra, due to protons, is eliminated by high-power proton decoupling; when this is carried out under the Hartmann-Hahn condition, ^{13}C - ^1H cross polarization occurs, which enhances the ^{13}C signal intensity and largely overcomes the problem of long ^{13}C relaxation times.³ The primary line-broadening effect that would remain, chemical shift anisotropy, is eliminated by rapid spinning (2.2 to 2.6 kHz) of the solid sample about an axis tilted at $54^\circ 44'$ (the magic angle) relative to the direction of the static magnetic field of the instrument.⁴⁻⁷ Under rapid magic-angle-spinning conditions, the ^{13}C resonance lines that are obtained are essentially what one would expect of a corresponding nonviscous liquid sample. Examples of the type of spectra one might expect for a pure (chemically homogeneous) sample are shown in Figures 1 and 2. For a complex chemical mixture, such as coal or oil shale, one may still expect to obtain broad resonance peaks, as is usually found to be the case in experimental results (Figures 3 and 4). The reason for the broad peaks is the presence of a large number of chemically similar species present in the sample, for which the (isotropic) chemical shifts and resonance positions are close together and cannot be resolved even under conditions of reasonably high resolution. The typical result for a coal or oil shale sample is a broad peak due to aromatic and olefinic carbons and another broad peak due to aliphatic carbons (Figures 3 and 4).

The specific experimental approach that we have employed in this work is a single-contact technique based on the more general experiment originally described by Pines, Gibby and Waugh.³ A 90° ^1H pulse is applied, followed by a 90° phase shift, after which the ^1H rf power is maintained during the ^1H - ^{13}C cross polarization and for ^1H decoupling during ^{13}C data acquisition. Radiofrequency power at the ^{13}C resonance frequency (at a level determined by the Hartmann-Hahn condition) is applied during the contact period (1-8msec), then turned off during the period in which the ^{13}C free induction decay (FID) is observed.

Our experiments were carried out at 15.1 MHz on a home-built spectrometer, based upon a 14-kgauss Varian 12-in magnet and a JEOL EC-100 Fourier transform data system. The Hartmann-Hahn condition was achieved with a 40 gauss H_1 field for ^{13}C and a 10-gauss H_1 field for ^1H . The spinning rates of 2.2-~~to~~-2.6 kHz were achieved with a spinner of the general Andrew-type,³ using 14 lb/in² pressure from a "house" air supply. Higher spinning speeds could be achieved with higher pressures and/or helium. The spinner contained about 1.1 cm³ of sample.

As can be seen in Figures 1-4, a great deal of structural detail is available in the spectra of solid pure substance, while for coal and oil shale, only broad bands are obtained. In some cases these bands contain "hints" of fine structure (e.g., bumps and shoulders), which should become more distinct in a high-field spectrometer. Even in the 14-kgauss spectra of the type shown in Figures 3 and 4, clear separations between the aromatic/olefinic and aliphatic resonances are achieved. This is in contrast with the overlapping resonance bands of spectra obtained without magic-angle spinning, in which chemical shift anisotropies cause overlapping of the resonances from these different structural classes of carbons.^{7,9,11}

From ^{13}C nmr spectra of the type shown in Figures 3 and 4, one can hope to make quantitative determinations of aromatic/olefinic and aliphatic carbon contents. However, many questions must be raised to determine the reliability of the above-mentioned approach for quantitative analytical purposes. These questions revolve largely about the dynamics of the experiment, i.e., the characteristic relaxation times of the pertinent processes (^1H and ^{13}C relaxation in the rotating frame, ^{13}C - ^1H cross polarization, ^1H and ^{13}C spin-lattice relaxation). The essential question is: can experimental conditions and corrections be found so that all organic carbon types are "counted" equally in the ^{13}C experiment? Many experiments have been carried out to characterize the conditions for typical coals and oil shales, so that optimized experiments could be designed. Comparisons with experiments carried out with high-power ^1H decoupling, but without ^{13}C - ^1H cross polarization, are essential for assessing the efficiency and deviations from uniformity of the cross polarization process. Success in optimizing the experimental conditions for determining aromatic/olefinic and aliphatic carbon contents determines the scope and accuracy of the approach. One key feature of calibrating the ^{13}C approach so that absolute aromatic/olefinic or aliphatic carbon contents can be determined is an external ^{13}C standard. The requirements for an external standard involve both the chemical shift (to avoid critical peak overlaps) and relaxation times (to avoid intensity distortions).

With a method capable of determining aromatic/olefinic and aliphatic carbon contents, various comparisons and correlations are possible. These include comparisons among related samples (e.g., oil shale and shale oil; coal and solvent-refined coal or hydrogenated coal), and correlations with pertinent fuel parameters, e.g., gal/ton obtained from oil shale or BTu/ton for coal or oil shale.

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Figure Captions

- Figure 1. ^{13}C nmr spectrum of catechin, obtained at 15.1 MHz under conditions of high-power ^1H decoupling, ^1H - ^{13}C cross polarization and magic-angle spinning. Spectral width 530 ppm, higher shielding to the right.
- Figure 2. ^{13}C nmr spectrum of polymethylmethacrylate, obtained at 15.1 MHz under conditions of high-power ^1H decoupling, ^1H - ^{13}C cross-polarization and Magic-angle spinning. Spectral width 530 ppm, higher shielding to the right.
- Figure 3. ^{13}C nmr spectrum of coal (Indiana), obtained at 15.1 MHz under conditions of high-power ^1H decoupling, ^1H - ^{13}C cross polarization and magic-angle spinning. Spectral width 530 ppm, higher shielding to the right. Spinning sidebands are marked with arrows.
- Figure 4. ^{13}C nmr spectrum of New Zealand shale, obtained at 15.1 MHz under conditions of high-power ^1H decoupling, ^1H - ^{13}C cross polarization and magic-angle spinning. Spectral width 530 ppm, higher shielding to the right.



Figure 1

D-GATECHIN
500 scans

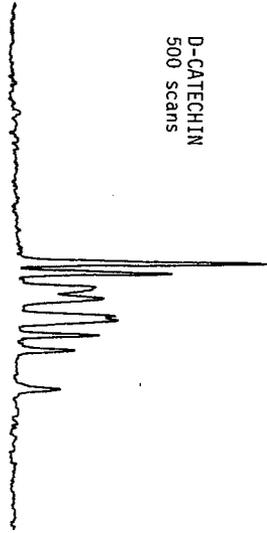


Figure 3

INDIANA BITUMINOUS
COAL
3000 scans

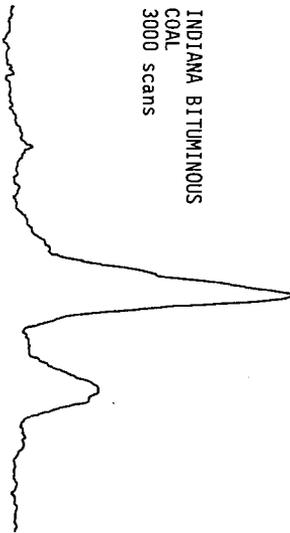


Figure 2
POLY(METHYL METHACRYLATE)
500 scans

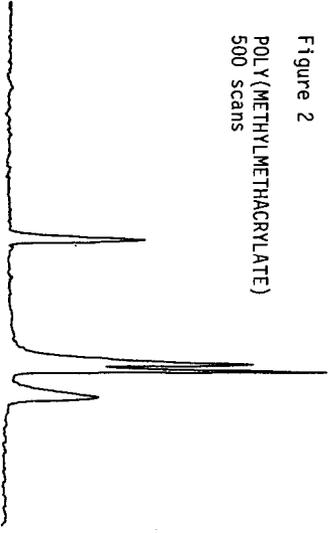
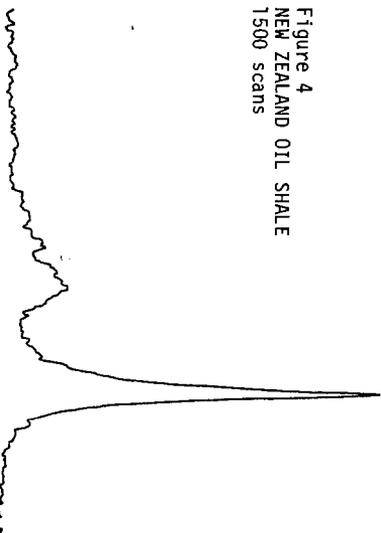


Figure 4
NEW ZEALAND OIL SHALE
1500 scans



8KHz (530 ppm)