

## NEW METHOD FOR MEASURING THE GRAPHITE CONTENT OF ANTHRACITE COALS AND SOOTS

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### Introduction

The amount of graphite-like structure of anthracitic coals and soots is an important parameter for understanding the composition of these materials. The structure of graphite has been studied extensively<sup>1-6</sup>, and is described by the delocalization of the  $\pi$  electrons over the carbon structure. These delocalized  $\pi$  electrons contribute to the conductivity of graphitic material. A recently proposed structure of coals<sup>7</sup> and soots consists of regions or clusters that are graphite-like in nature, linked by non-conductive chain/bridging regions. The electrical conductivity of these materials will therefore depend on the extent of these graphitic regions. Therefore, by measuring the electrical conductivity of these samples it is possible to estimate the amount of graphitic materials present.

The direct measurement of electrical conductivity is a classical method<sup>8</sup> in which a pair of electrodes is placed across the sample. However, due to the low resistivity ( $1.5 \times 10^{-3}$  ohm-cm),<sup>9</sup> the resistance of the electrical contact between the electrodes and the sample could seriously affect the measurement results, especially when the sample is a powder. In addition, the heterogeneity of the samples and the presence of nonconductive regions make it difficult to measure the electrical conductivity of the sample in this manner. In order to solve such problems, the method of measuring the quality factor (Q value) of a radio frequency (RF) coil at high frequency has been employed.<sup>10,11</sup>

A Q meter is used to measure the Q value of a RF coil which is defined by:

$$Q = 2\pi fL/R \quad (1)$$

where,  $f$  is the applied frequency,  $R$  is the resistance of the coil at this frequency, and  $L$  is the inductance of the coil. When a sample is placed inside the coil, any conduction electrons in the sample will be driven into motion by the electric field induced by the high frequency magnetic field inside the coil according to the Faraday Law<sup>12</sup>.

$$\nabla \times E = -\partial B / \partial t \quad (2)$$

The interaction of moving electrons with the graphite lattice leads to an energy loss. This energy loss inside a coil results in a decrease in the Q value of the coil and therefore a resultant increase in resistance. The  $\Delta Q$  between an empty and a sample filled coil is directly proportional to  $\Delta R$ . Since  $\Delta R$  is a measure of the delocalized electron content, it is also a reflection of the graphitic carbon content of the sample.

Experimentally, the correlation between  $\Delta Q$  and the graphitic carbon content can be obtained by performing the measurement on a series of standard samples where pure graphite is diluted with silica gel of known composition. The graphitic carbons content in the unknown sample, i.e., the coal or soot, can then be estimated by determining  $\Delta Q$  on a sample of known mass.

### The Principle of the Measurement

The Q value of an RF coil is measured with a Q meter, a classical electrical instrument.<sup>13</sup> Let  $Q_0$  be the value of the empty coil. The value of  $Q_0$  decreases to  $Q_i$  when a sample that contains conductive material is placed inside the coil, but the inductance  $L$  remains essentially the same (less than 1% change). The energy loss due to the moving conduction electrons interacting with the graphite lattice causes an increase in the resistance from  $R$  to  $R + \Delta R$  with a corresponding decrease in the quality factor from  $Q_0$  to  $Q_i$  and

$$Q_i = 2\pi fL / (R + \Delta R) \quad (3)$$

Equation 3 can be rewritten as

$$Q_i = 2\pi fL / R(1 + \Delta R/R) = Q_0 / (1 + \Delta R/R) \quad (4)$$

For the coil used in this study at  $f = 100$  MHz,  $Q_0 = 258$ ,  $L = 0.145 \mu\text{H}$  and the calculated value of  $R$  is  $0.353 \Omega$ . Substituting these data into equation 4 gives:

$$Q_i = 258 / (1 + \Delta R / 0.353 \Omega) = 258 / (1 + \Delta R 2.83 \Omega^{-1}) \quad (5)$$

A plot  $Q_i$  vs  $\Delta R$  results in a hyperbolic curve with a vertical asymptote at  $\Delta R = -0.353 \Omega$ . Inverting both sides of equation 5 yields the linear relationship:

$$1/Q_i = (1 + \Delta R 2.83 \Omega^{-1}) / 258 = 0.00388 + \Delta R 0.011 \Omega^{-1} \quad (6)$$

Recognizing that  $\Delta R$  is much less than  $1 \Omega$  a Taylor series expansion ( $1/(1+x) \cong 1-x$ ) yields equation 7:

$$Q_i = 258(1 - \Delta R 2.83 \Omega^{-1}) \quad (7)$$

As mentioned earlier  $\Delta R$  is proportional to the  $G$ , the quantity of graphite (mg) in this limited volume of sample. Therefore,  $G$  can be represented by:

$$G = K \Delta R \quad (8)$$

By obtaining a series of  $Q_i$  and  $\Delta R$  values from a set of samples with known graphite concentration the coefficient  $K$  can be obtained and a linear relationship between  $Q_i$  and  $G$  can be written as:

$$Q_i = 258[1 - (G/K) 2.83 \Omega^{-1}] \quad (9)$$

which can be rearranged to:

$$G = -1.37 \times 10^{-3} Q_i K \Omega + 0.353 K \Omega \quad (10)$$

The practical form of equation 10 will be discussed in the next section.

### Experimental Details

A Q meter (Type 170A, Boonton Radio Corporation U. S. A.) was used for measuring the Q value of a RF coil. The operating frequency was 100MHz for reasons of convenience, coil size and Q measurement sensitivity. A five-turn solenoid coil of inside diameter 0.83 cm, and length 1.40 cm, wound from 16-swg copper wire was used for the experiments. The inductance of this solenoid coil is  $0.145 \mu\text{H}$  and at 100MHz the Q value is 258.

Each sample was placed in a zirconia solid-state rotor (Chemagnetics, Inc.). In each measurement a constant volume of sample ( $0.33 \text{ cm}^3$ ) was used which filled to solenoid. A set of standard samples was prepared by mixing pure graphite powder (Aldrich Catalogue NO: 28286-3) with silica gel (Aldrich Catalogue NO: 28859-4). The value of  $Q_i$  is silica gel independent. The standard and test samples occupied the same volume. Care was taken to place the sample in the sample holder such that the entire sample was within the coil for the Q measurement. The mass of each sample was also recorded.

The measurements of the unpaired electron concentration in each sample were made on a Bruker ESR spectrometer. Experimental details of the measurement will be discussed in a subsequent paper. All NMR measurements were obtained on a Chemagnetics CMX-100 spectrometer using a PENCIL rotor spinning system under conditions described previously.<sup>14</sup> All experiments were carried out at room temperature.

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## Results and Discussion

Table 1 contains the  $Q_i$  values associated with the standard samples of varying graphite content. The least squares fit of the data is:

$$G \text{ (mg)} = -0.69917Q_i + 182.30 \quad (11)$$

This is the form of equation (10) and is used to calculate the graphite content of test samples. The graphite factors in Tables 3 and 4 are the values derived from equation 11 normalized by the weight of the sample.

Four anthracitic coals (LCNN, Jeddo, UAE and Summit) obtained from The Pennsylvania State University were used in this study. The elemental analysis is provided in Table 2. The measured  $Q_i$  values, the graphite content, the atomic ratios C/H and the concentration of the unpaired electrons are given in Table 3. Similar information for several soot samples is given in Table 4.

This method has been applied for the first time to measure the graphite-like structures in the anthracites and soot samples. Both of these materials are of complex composition containing mixtures of both amorphous and semi-ordered structures and, as far as the investigators can determine, no data of this type have previously appeared in the literature. However, based on some results from other experiments, a possible qualitative explanation will be discussed as below.

The data in Table 3 indicate that the differences in graphitic carbon content of the four anthracites is significant, i. e., by an order of magnitude when one compares the data of the LCNN and Summit samples. However, the concentration of unpaired electrons in these four samples is essentially constant, varying by less than a factor of 2. The graphite factor in the anthracite sample with the highest concentration of unpaired electrons (UAE) is only 0.024. These results indicate that not all measured unpaired electrons contribute to the electrical conductivity. No change in the  $Q$  value of a coil is observed when a stable free radical such as DPPH (a standard free radical sample) is placed in the coil. These data indicate that there are at least two different types of electrons in the systems under study; 1) electrons such as found in DPPH where the electron is localized and, 2) electrons that can occupy conduction bands in graphite type structures made up of extended hexagonal ring systems. These extended ring systems may contain, especially in the soot samples, some five-member rings.<sup>15</sup>

It is still not clear what size hexagonal ring systems is large enough to exhibit conduction behavior. For example, coronene, which has seven rings, has no effect on the  $Q$  value of the RF coil. Celzard<sup>7</sup> proposed that at least 70 hexagonal rings and a C/H weight ratio higher than 50 (atomic C/H  $\approx$  4.2) is where conductive behavior starts. According to the data shown in Table 3 the atomic C/H ratio of the anthracite coals from LCNN to Summit is 5.35, 4.44, 3.59, and 3.13, respectively. Comparison of these data with the graphitic carbon content seems to be reasonably in line with the results of Celzard.

The <sup>13</sup>C MAS spectra of four of the samples examined in this study are shown in Figure 1. The spectra of two anthracites and the anthracene soot residue were obtained using the CP technique. The diesel soot spectrum was taken with the single pulse technique due to a depletion of protons in the sample which renders the CP technique ineffective. These four samples have quite different percentages of the graphitic carbon. The graphite-factors for the four samples are: 0.014, 0.148, 0.48 and 0.61 for Summit, LCNN, the 1400 K anthracene soot residue and diesel soot #4, respectively. One can see that there is a great variation of line widths among the four samples that, to some degree, follows the graphite factor. The increased line width is due to anisotropy of the magnetic susceptibility of regions of graphene layering that is not totally removed under MAS

conditions.<sup>16,17</sup> The Summit sample has the appearance of a normal diamagnetic sample with a very small graphite factor and no unusual line broadening. While the line width (FWHM) of the LCNN is essentially the same as that of the Summit, some line broadening appearing as Lorentzian are evident in the LCNN sample. The anthracene soot residue has even broader wings and the broadening of the main resonance is approximately 40% than that of the LCNN. The diesel engine soot has an extremely broad resonance, which is also noted in samples so deficient in proton content that the CP experiment is not effective.<sup>14</sup>

## Conclusion

A rather simple method seems to be useful for correlating sample conductivity with the presence of graphene layering in graphitic carbon structures in anthracitic coals and numerous soot samples. The technique reported is useful for estimating the amount of graphite like structures in amorphous carbonaceous samples. It has been demonstrated that the number of unpaired electrons, per se, may not be a reliable parameter for estimating either sample conductivity or the extent of graphitization of soot samples. By utilizing a radio frequency coil one can induce a high frequency electric field in the sample and thus avoid any physical contact with the sample. This technique renders the experimental results free from any of the classical problems associated with electrical contact at the surface. The data indicate that the concentration of free radicals in the sample is not a reliable indication of either the conductivity of the sample or the amount of graphitic carbon present. High resolution TEM data indicate that different levels of ordered structures exist in many of the samples that we have examined and an analysis of the relationship between structure and conductivity will be attempted.

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**Table 1. The  $Q_i$  value associated the samples with different graphite content.**

Sample	Sample Weight (mg)	Graphite Content (mg)	Graphite (%)	$Q_i$ Value <sup>a</sup>
1	181.9	60.3	33.2	182.4
2	185.2	36.5	19.7	199.2
3	167.3	24.2	14.5	222.0
4	177.6	17.2	9.68	242.2
5	182.7	8.6	4.7	248.2
6	193.2	5.8	3.0	252.0
7	193.0	4.2	2.2	254.4

a) The frequency of the measurement was 100MHZ; at this frequency the  $Q$  value of the empty coil is 258.

**Table 2. Elemental analyses of the anthracite coal samples.**

Sample	C (%)	H (%)	N (%)	S (%)	O (%) (by diff)
LCNN	95.7	1.5	1.2	0.5	1.0
Jeddo	95.2	1.8	1.1	0.6	1.3
UAE	94.0	2.2	1.0	0.5	2.3
Summit	93.2	2.5	1.6	0.6	2.2

**Table 3. The measured graphite-factor, C/H atomic and mass ratios,  $Q_i$  measurement, and spin concentration of unpaired electrons of the anthracite coal samples.**

Sample	Graphite Factor	Atomic C/H	C/H Weight Ratio	$Q_i$ Value <sup>a</sup>	Spin Concentration ( $10^{19}$ spins/g)
LCNN	0.148	5.35	63.8	184	3.3
Jeddo	0.112	4.44	52.9	200	3.5
UAE	0.024	3.59	42.7	250	4.9
Summit	0.014	3.13	37.3	254	2.6

a) The frequency of the measurement was 100MHz; at this frequency the Q value of the empty coil is 258.

**Table 4. The measured graphite-factor and unpaired electron spin concentration of some soot samples.**

Sample	Sample Weight (mg)	Graphite Factor	$Q_i$ Value <sup>a</sup>	Spin Concentration ( $10^{19}$ spins/g)
Anthracene 1400 K Soot Residue	163	0.48	148.8	11.00
Diesel Soot Residue <sup>b</sup>	192	0.43	143.0	0.87
Ethylene Soot Residue <sup>b</sup>	150	0.48	157.0	3.78
NIST DPM 1650 Residue <sup>b</sup>	180	0.34	172.0	1.11
Diesel Soot #1	174	0.47	141.0	3.99
Diesel Soot #3	177	0.28	150.0	3.60
Diesel Soot #4	186	0.61	123.0	3.82
Diesel Soot #5	186	0.61	124.0	3.00

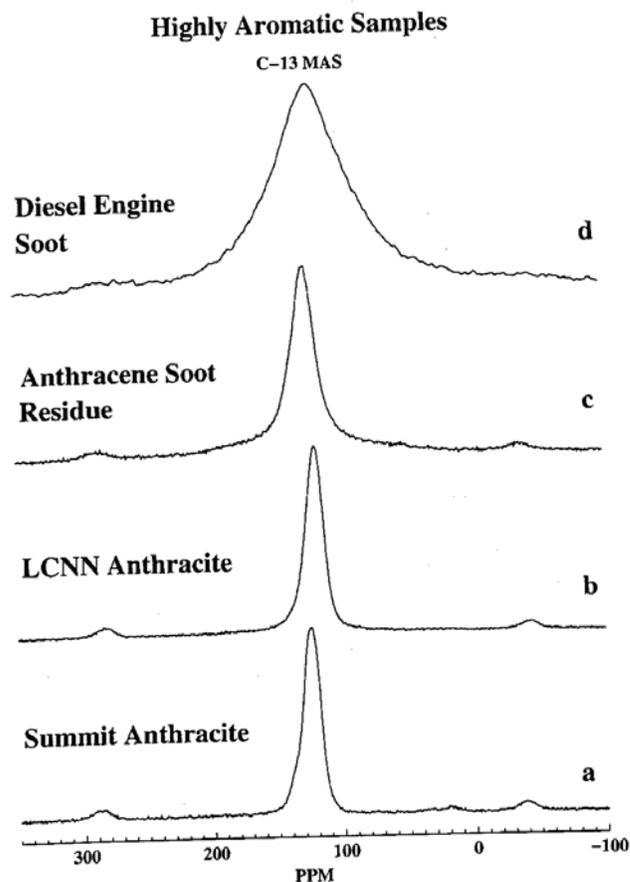
a) The frequency of the measurement was 100MHz; at this frequency the Q value of the empty coil is 258.

b) Residue is the insoluble part after 24 hrs extraction with dichloromethane in a Soxhlet extraction system.

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**Figure 1.**  $^{13}\text{C}$  MAS spectra of four of the samples. The spectra in a, b, c were taken with the CP technique all with a 1 s pulse delay. a) 3 ms contact time b) 10 ms contact time, c) 10 ms contact time d) spectrum taken with the single pulse method and using a 10 s pulse delay.