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Determination of the fraction of paramagnetic centers not-fulfilling the Curie law in coal macerals by the two-temperature EPR measurement method

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Abstract. Two-temperature electron paramagnetic resonance (EPR) measurements, applied to determine the relative contributions of paramagnetic centers – fulfilling and not-fulfilling the Curie law, were carried out. The measurements were made on the macerals – exinite and vitrinite, separated from clarain of the Polish medium--rank coal (85.6 wt% C). The two-temperature EPR measurements, presented in this work, were performed respectively, at temperatures: $T_1 = 293$ K and $T_2 = 173$ K for exinite, and $T_1 = 293$ K and $T_2 = 153$ K for vitrinite. The relative contributions X of spins not-fulfilling the Curie law present in the studied macerals were calculated. A comparison of different methods of calculating the relative contributions of paramagnetic centers – fulfilling and not-fulfilling the Curie law, present in exinite and vitrinite studied by EPR was made.

Key words: electron paramagnetic resonance (EPR) • macerals • two-temperature EPR measurement

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Introduction

While examining coal, the characteristics of its physicochemical properties and the structure, appear to be one of the main problems faced. The study of the existing relationship between the structure and properties of the remains from coal processing also constitutes one of the most important problems. The structure of coal can be described in terms of models, which are presented at the following three levels:
1. the petrographic structure (macerals, inorganic matter),
2. the macromolecular structure (macromolecular and low-molecular phases),
3. the chemical structure (aliphaticity and aromaticity, average chemical structural units).

The concept of macerals is the most often applied one for describing the petrographic structure of coal.

The macerals, exinite, vitrinite, and inertinite, are the basic petrographic components of coal. Their properties are dependent on the coal rank with disordered internal structure. Exinite, vitrinite, and inertinite are microscopically distinguishable ones – on the basis of the reflectivity of light and their color.

They are present in coal macerals, exinite and vitrinite, in multiwalled carbon nanotubes (MWNT), in ancient silk textiles, in pyrolytic graphite, and in pulverized coal groups of paramagnetic centers fulfilling and not-fulfilling the Curie law (given in the form $I = C/T$). In our study of the coal macerals, ex-

inite and vitrinite, performed by the two-temperature EPR measurement method, we aimed to determine the relative contribution X of the paramagnetic centers not-fulfilling the Curie law and to compare them with the X values for thermally decomposed coal macerals.

Two-temperature EPR measurement is a method used for determining the relative contributions of localized and delocalized spins present in studied paramagnetic coal samples. Measuring the EPR line intensities I in two different temperatures T_1 and T_2, allows to determine the contribution X of paramagnetic centers not-fulfilling the Curie law present in studied samples.

This method was used in the EPR examination of MWNT [1]. In that work [1], mixed Curie- and Pauli-like temperature dependence of EPR line intensity was assumed to estimate the contribution of delocalized π-electron states in resonance. It was found [1] that about 80% spins are delocalized.

Two-temperature EPR measurement method was also used to study a series of nine samples of pyrolytic graphite annealed in the temperature range 1973–2873 K [2]. The biggest value $X = 0.996$ of the relative contributions of delocalized spins was calculated for pyrolytic graphite samples with the highest temperature of annealing (2873 K) [2]. In the work, where MWNT by two-temperature measurement method [1] was studied, the authors explained the differences between the values of X obtained for MWNT and values of X obtained for pyrolytic graphite, using the same method [2] tubular geometry of graphene layers, which determine the formation of conduction π-electrons [1].

In the Appendix, the derivation of the formula for two-temperature EPR measurement method is given [3]. We denote total intensity of EPR line I [a.u.] in temperature T_1 [K] by $I_1 = I_{NC}(T_1) + C/T_1$ (C – Curie constant [K]) and in temperature T_2 by $I_2 = I_{NC}(T_2) + C/T_2$, respectively, where $I_{NC}(T)$ is a part of total intensity I generated by paramagnetic centers, which do not fulfil the Curie law, while the paramagnetic centers obeying the Curie law are responsible for the component C/T. The existence of paramagnetic centers in the ground doublet state $S = \frac{1}{2}$, for which the temperature dependence of intensity is described by the Curie law ($I = C/T$) (and paramagnetic centers in excited triplet states ($S = 1$) was evidenced in coal and coal macerals [4–9].

Two-temperature EPR measurements were carried out also for a series of samples of irradiated carbon blacks [10]. For each of the carbon black samples examined by EPR in that work, the values X were calculated with the formula: $R = 0.88X + 3.65(1 - X)$, where $R = (I_{LN})/(I_{RT})$ denotes the ratio of intensities I_{LN} and I_{RT}, respectively, at temperatures: $T_{LN} = 80$ K and $T_{RT} = 293$ K [10].

Another way of determining the relative contributions of different types of paramagnetic centers in singlet ($S = 0$), doublet ($S = \frac{1}{2}$), and triplet ($S = 1$) states, existing in studies of EPR samples, is possible. This method was used during examination of spin excitations of bitumens [11] and in searching of triplet states in DOPA-melanin and its complexes

with kanamycin and copper Cu(II) ions [12]. The mathematical formula describing the temperature dependence of EPR line intensity I_d connected with the paramagnetic centers in doublet state ($S = \frac{1}{2}$) is presented in the form of the Curie law [11]:

$$(1) \qquad I_d = \frac{aN_d}{2kT}$$

where I_d – line intensity generated by paramagnetic centers in doublet state ($S = \frac{1}{2}$), a – constant, N_d – number of paramagnetic centers in doublet state ($S = \frac{1}{2}$), k – Boltzmann constant [J/K] and T [K] – temperature of measurement. The temperature behavior of the EPR line intensity connected with paramagnetic centers in triplet state ($S = 1$) is given by the formula derived by Bleaney & Bowers [13]:

$$(2) \qquad I_t = \frac{2aN_{s-t}}{kT\left(e^{\frac{J}{kT}} + 3\right)}$$

where I_t denotes the line intensity generated by paramagnetic centers in triplet state ($S = 1$), N_{s-t} is a sum of the number of centers in singlet ($S = 0$) and triplet states ($S = 1$), and J [K] is the excitation energy singlet-triplet. Total intensity of EPR line taking into account the existence of paramagnetic centers in singlet and triplet states is presented in the form [12]:

$$(3) \qquad I = I_d + I_t = \frac{C}{T} + \frac{B}{T\left(e^{\frac{J}{kT}} + 3\right)}$$

where B and C [K] are constants equal to

$\dfrac{2aN_{s-t}}{k\left(e^{\frac{J}{kT}} + 3\right)}$ and $aN_d/2k$, respectively [12].

Accordingly, relative contributions of paramagnetic centers in singlet ($S = 0$) and triplet ($S = 1$) states to whole amount of centers in doublet, singlet, and triplet states are given in the form [12]:

$$(4) \qquad \frac{N_{s-t}}{N_d + N_{s-t}} = \frac{\dfrac{B}{C}}{4 + \dfrac{B}{C}}$$

As mentioned earlier, it was shown [6–9] that in the total group of paramagnetic centers generating components lines in the form of Lorentzian L1 shape in EPR spectra of coal macerals, exinite, and vitrinite, there is a part of centers in excited triplet state ($S = 1$). Accordingly, these centers do not fulfil the Curie law represented by the formula $I = C/T$. Their contribution to the total intensity is described by the formula:

$$(5) \qquad I = \frac{B}{T\left(e^{\frac{J}{kT}} + 3\right)}$$

The fraction of paramagnetic centers in excited triplet state in the total number of paramagnetic centers changes with temperature T.

Experimental

Coal macerals, exinite, vitrinite, and inertinite, studied by EPR in this work were obtained from Polish medium-rank coal (85.6 wt% C) from 1 Maja Coal Mine in the Upper Silesian Coal Basin and characterized by very high purity (75 vol.%, 90 vol.%, respectively). Densities d of macerals (in g/cm³) were respectively: $d < 1.24$ for exinite, $d = 1.28 \div 1.30$ for vitrinite, and $d > 1.36$ for inertinite. Exinite, vitrinite, and inertinite were separated by centrifugation of the demineralized clarain, one of the lithotypes of coal (except durain and vitrain), in toluene-carbon tetrachloride mixtures. Maceral samples, examined in this work, were placed in thin-wall glass tubes, evacuated to 10^{-4} Torr (pumping time $t = 24$ h) and sealed, in order to avoid interactions between

Fig. 1. Deconvolution of the EPR spectra of exinite, vitrinite and inertinite ($T = 291$ K).

molecules of atmospheric oxygen and paramagnetic centers present in exinite, vitrinite, and inertinite. The two-temperature EPR measurements of exinite and vitrinite were performed using an EPR spectrometer of S/EX type produced by Radiopan (Poznań, Poland). The microwave radiation frequency was 9.3 GHz and the magnetic field modulation 100 kHz. The amplitude of modulation frequency was 0.02 mT. The microwave power used in two-temperature EPR measurements to avoid signal saturation of examined exinite and vitrinite was 0.7 mW by maximum microwave power generated by klystron about 70 mW. Attenuation of microwave power used in the measurement ranged 0–20 dB.

The temperature system used in this work during the temperature measurements was equipped with an electronic temperature stabilizer, which allows to obtain predetermined measuring temperatures with high accuracy.
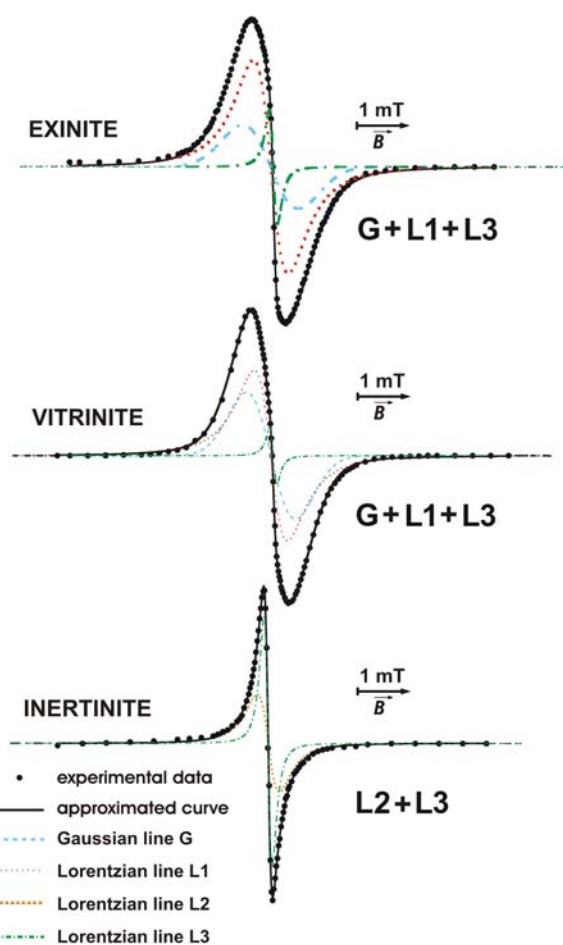
Results and discussion

In this work, the EPR study of coal macerals, exinite, vitrinite, and inertinite, by the two-temperature measurement method was performed. In Fig. 1, the EPR spectra of the three macerals exinite, vitrinite, and inertinite are shown. The spectra underwent deconvolution into four component lines of Gaussian (G) and/or Lorentzian (L1, L2, L3) lineshape with different linewidths ΔB_{pp} fulfilling the inequalities $\Delta B_{pp}(G) > \Delta B_{pp}(L1) > \Delta B_{pp}(L2) > \Delta B_{pp}(L3)$. The EPR spectra of exinite and vitrinite consist of three lines: one line with Gaussian lineshape (G) and two lines with Lorentzian lineshape (L1, L3). The EPR spectrum of inertinite consists of two lines with Lorentzian lineshape (L2, L3). The measured values of linewidths ΔB_{pp} measured at temperature 291 K and with attenuation 20 dB were: for exinite 0.95 mT (G), 0.59 mT (L1), 0.14 mT (L3); for vitrinite 0.88 mT (G), 0.59 mT (L1), 0.12 mT (L3); and for inertinite 0.32 mT (L2), 0.12 mT (L3). It is only the Lorentzian line L1 from these four component lines (G, L1, L2, L3) that does not fulfil the Curie law. Because inertinite does not contain paramagnetic centers not-fulfilling the Curie law, it was not studied further.

The two-temperature EPR measurements were carried out at $T_1 = 293$ K and $T_2 = 173$ K for exinite and at $T_1 = 293$ K and $T_2 = 153$ K for vitrinite, respectively. The results of calculation for the values of fractions X are shown in Table 1. The values of D_{NC}

Table 1. Values of the total EPR line intensity I, EPR line intensity of centres not-fulfilling the Curie law I_{NC} for the component EPR line with Lorentzian lineshape (L1) of the coal macerals, exinite and vitrinite, the parameter D_{NC} and the fraction X of paramagnetic centres not-fulfilling the Curie law in relation to the sum of paramagnetic centres not fulfilling the Curie law and paramagnetic centres obeying the Curie law calculated with the two-temperature EPR measurement method

Sample	Temperature, T [K]	Total intensity, I [a.u.]	Partial intensity, I_{NC} [a.u.]	Parameter D_{NC}	Fraction X
Exinite	$T_1 = 293$	4.92	1.773	0.689	0.36
	$T_2 = 173$	6.55	1.221		
Vitrinite	$T_1 = 293$	4.52	0.750	0.125	0.17
	$T_2 = 153$	7.32	0.093		

Table 2. Values of constants C and B in Eq. (3) for the component EPR line with Lorentzian lineshape (L1) of the coal macerals, exinite and vitrinite, and the fraction of the centres in singlet ($S = 0$) ant triplet ($S = 1$) states in relation to the sum of the centres in doublet ($S = \frac{1}{2}$), singlet and triplet states $N_{s-t}/(N_d + N_{s-t}) = B/(4C + B)$

Sample	C [a.u.]	B [a.u.]	Fraction $N_{s-t}/(N_d + N_{s-t}) = B/(4C + B)$
Exinite	0.922	4.41	0.54
Vitrinite	1.106	5.61	0.56

for the studied macerals, calculated from the formula (11), are 0.689 for exinite and 0.125 for vitrinite, and they denote the line intensity ratio $[I_{NC}(T_2)/I_{NC}(T_1)]$ of paramagnetic centers, which do not fulfill the Curie law, measured at temperatures T_1 and T_2.

The values of the relative contribution X of paramagnetic centers, which do not fulfil the Curie law in exinite and vitrinite at room temperature ($T_1 = 293$ K) calculated by using the formula (12), are as follows: $X = 0.36$ (exinite) and $X = 0.17$ (vitrinite).

The values $[(N_{s-t}/(N_d + N_{s-t})]$ calculated on the basis of formula (4) are nearly equal to 0.54 for exinite and 0.56 for vitrinite, respectively (Table 2).

Results obtained in this work for nonheated coal macerals, exinite and vitrinite, correlate well with earlier results obtained by Pilawa [3] for coal macerals heated at 573–923 K. The values of X determined by Pilawa were 0.32 and 0.28 (exinite heated at 573 and 923 K) and 0.41 and 0.50 (vitrinite heated at 573 and 923 K), respectively.

The existence of paramagnetic centers in thermally excited triplet state ($S = 1$) in the whole group of paramagnetic centers present in exinite and vitrinite is one of several models explaining the observed temperature dependence of EPR line intensity. However, in another model for the deviation from Curie law for earlier mentioned coal macerals, delocalized π-electrons of aromatic units can be responsible, which is indicated by results of the two-temperature EPR measurement [1].

Almost identical EPR lines (similar g factor, linewidth ΔB_{pp} [T], and asymmetric spectral shape), which were generated by paramagnetic centers presented in non-heated exinite and vitrinite, were obtained during EPR examination of ancient silk textiles [14]. It suggests that in studies of ancient silk textiles there are also paramagnetic centers in singlet, doublet, and triplet states similar as in coal macerals. The studies presented in the mentioned paper [14] provide input to the knowledge about their degradation mechanism.

Besides, the analysis of EPR spectra of superfine pulverized coal [15] showed the existence of four groups of paramagnetic centers in the studied samples, similar to the four groups of paramagnetic centers present in the coal macerals. According to the authors, the EPR spectra of the studied superfine pulverized coal [15] are the superposition of components lines generated by different groups of paramagnetic centers. The lines can be fitted by one Gaussian and three Lorentzian lines. This interpretation of complex EPR spectra of coal and coal macerals was given earlier by Więckowski and coworkers [3–9].

Conclusions

On the basis of the current work and the results obtained earlier by Pilawa [3], we can note that the values of X decreases with an increase in temperature of the thermal decomposition of the studied macerals, resulting in the greatest value for nonheated exinite. On the other hand, X raises with an increase in temperature of the thermal decomposition for vitrinite, resulting in the smallest value for nonheated vitrinite.

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Appendix

We can create the relationship

$$(6) \qquad \frac{I_2}{I_1} = \frac{I_{NC}(T_1) + \dfrac{C}{T_2}}{I_{NC}(T_1) + \dfrac{C}{T_1}} = \frac{I_{NC}(T_2)}{I_{NC}(T_1) + \dfrac{C}{T_1}} + \frac{\dfrac{C}{T_2}}{I_{NC}(T_1) + \dfrac{C}{T_1}}$$

for $T_1 = T_2$

$$(7) \qquad \frac{I_2}{I_1} = \frac{I_{NC}(T_1) + \dfrac{C}{T_1}}{I_{NC}(T_1) + \dfrac{C}{T_1}} = \frac{I_{NC}(T_1)}{I_{NC}(T_1) + \dfrac{C}{T_1}} + \frac{\dfrac{C}{T_1}}{I_{NC}(T_1) + \dfrac{C}{T_1}} = X + \frac{\dfrac{C}{T_1}}{I_{NC}(T_1) + \dfrac{C}{T_1}} = 1$$

where $X = \dfrac{I_{NC}(T_1)}{I_{NC}(T_1) + \dfrac{C}{T_1}}$ and this expression denotes contribution of delocalized electron states [3].

Next we have:

$$(8) \qquad 1 - X = \frac{\dfrac{C}{T_1}}{I_{NC}(T_1) + \dfrac{C}{T_1}}$$

$$(9) \qquad \frac{X}{I_{NC}(T_1)} = \frac{1}{I_{NC}(T_1) + \dfrac{C}{T_1}}$$

$$(10) \qquad \frac{I_1}{I_2} = \frac{X I_{NC}(T_2)}{I_{NC}(T_1)} + \frac{\dfrac{C}{T_2}}{\dfrac{C}{T_1}} = \frac{I_{NC}(T_2)}{I_{NC}(T_1)} X + \frac{T_1}{T_2}(1 - X) = D_{NC} X + \frac{T_1}{T_2}(1 - X)$$

where

$$(11) \qquad \frac{I_{NC}(T_2)}{I_{NC}(T_1)}$$

Finally, we have [3]:

$$(12) \qquad X = \frac{\dfrac{I_2}{I_1} - \dfrac{T_1}{T_2}}{D_{NC} - \dfrac{T_1}{T_2}} \ .$$