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**Applied Magnetic Resonance**



# Paramagnetic Centres in Exinite, Vitrinite and Inertinite

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**Abstract.** Exinite, vitrinite and inertinite from durain, vitrain and clarain of Polish medium-rank coal with 85.6% C were investigated by X-band (9.3 GHz) electron paramagnetic resonance spectroscopy. Multicomponent structure of the EPR spectra of these macerals was analysed. The number of component lines, their lineshapes and parameters: linewidths and $g$ factors, were determined. Total concentrations and concentrations of paramagnetic centres responsible for the component lines were measured. The broad Gaussian, broad Lorentzian and narrow Lorentzian lines were observed in the experimental spectra of exinite and vitrinite. The EPR spectra of inertinite are superposition of two narrow Lorentzian lines with different linewidths. The evolution of paramagnetic centres during heating of the macerals at 300–650°C was studied. Paramagnetic centres with broad Lorentzian lines are the most active ones in the thermal decomposition. The EPR results indicate reactions between individual macerals during thermal decomposition of coal. Thermally excited multiplet states were found in exinite and vitrinite.

## 1. Introduction

Organic substance of coal and macerals is characterized by high content of stable paramagnetic centres (~1017–1021 spin/g) [1–14]. Paramagnetic centres belonging to different chemical units are responsible for the observation of several lines in their EPR spectra [2–5, 13, 14]. The number of component lines in the total resonance absorption curves depends on the degree of coalification of the coal samples and the kind of maceral [4, 13, 14]. Electron paramagnetic resonance was used to study the evolution of paramagnetic centres in coal [15–20] and macerals [21–24] during thermal decomposition, but most of these works [15–20] refer to changes in the total spin population of the heated samples. The complex chemical structure of coal and macerals and complex character of their EPR spectra are responsible for the large difficulties in the investigation of role and changes in individual groups of paramagnetic centres in the process of thermal decomposition. The aims of the present work were to characterize different groups of paramagnetic centres of exinite, vitrinite and inertinite from medium-rank coal, to determine changes in their concentrations and properties during thermal decomposition of macerals and to search thermally excited multiplet states in heated macerals.

## 2. Experimental

### *2.1. Characteristics of the Investigated Maceral Samples*

Coal contains three lithotypes-banded constituents characterized by different types and degree of lustre: durain, vitrain and clarain. Lithotype means rock type, a rock being an assembly of minerals. Organic substance of coal is composed by three basic petrographic constituents differing in chemical and physical properties: exinite, vitrinite and inertinite, which are called macerals. The H/C atomic ratio decreases from exinite to inertinite. The oxygen content decreases in order: vitrinite > exinite > inertinite. The lowest and the highest relative contents of aromatic and aliphatic structures characterize exinite and inertinite, respectively. Density and reflectance increase from exinite to inertinite. Durain and clarain contain exinite, vitrinite and inertinite. Vitrain contains mainly vitrinite.

The macerals: exinite, vitrinite and inertinite, separated from lithotypes: durain, vitrain and clarain, of Polish medium-rank coal with 85.6% C, were investigated by EPR spectroscopy. The demineralized coal contains 9 vol% exinite, 77 vol% vitrinite, and 14 vol% inertinite. The macerals were separated by centrifugation of the demineralized lithotypes in toluene-carbon tetrachloride mixtures with required density. Preparation of the maceral samples was described earlier [14].

The maceral samples were heated for 40 min in an argon flow at temperatures ranging from 300 to 650°C at 50°C intervals. The loss of mass (wt%) of the heated samples was measured (Fig. 1). The loss of mass of the heated macerals considerably increases with temperature above 500°C. The highest and the lowest loss of mass were measured for exinite and inertinite, respectively (Fig. 1a, c).

The original and the heated samples were mixed with $SiO_2$ (1:5) and placed in thin-walled glass tubes. No EPR signal from impurities was observed in the empty tubes.

### *2.2. EPR Method*

The maceral samples in air and in vacuum ($10^{-4}$ Torr) were investigated by EPR at X-band with microwave frequency of 9.3 GHz and with magnetic modulation frequency of 100 kHz. The EPR spectra were obtained with high attenuation of microwave power of 20 dB (~0.7 mW) to avoid signal saturation. The lineshape of the EPR spectra was studied by Opfermann's numerical algorithm [25]. The experimental spectra were fitted by different superpositions

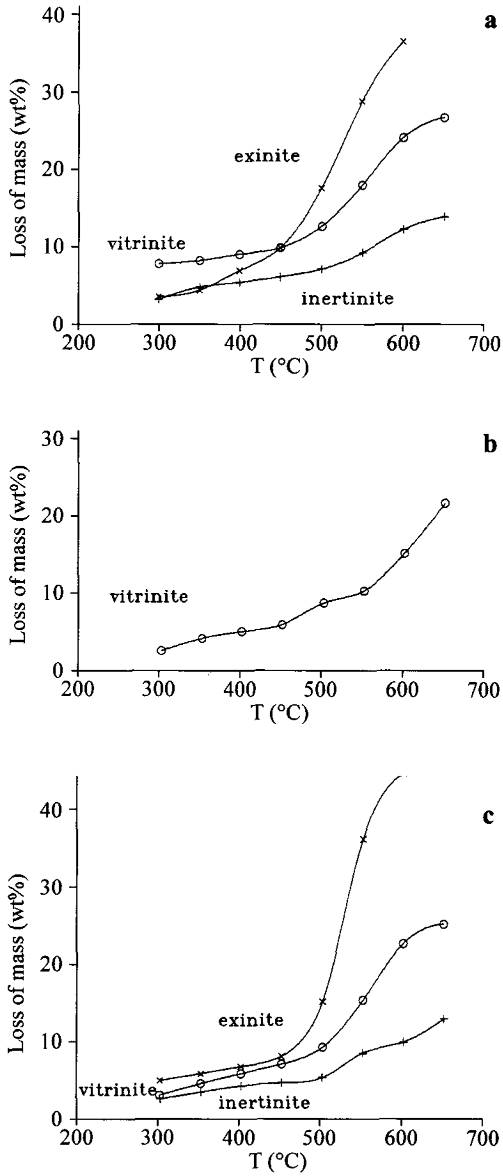


**Fig. 1.** **a** The loss of mass of macerals from durain heated at 300–650°C. **b** The loss of mass of vitrinite from vitrain heated at 300–650°C. **c** The loss of mass of macerals from clarain heated at 300–650°C.

of Gaussian and Lorentzian lines. As the best results of resonance curve fitting those approximations which gave the smallest value of the root-mean-square deviation were accepted. The parameters of the best-fit lines were calculated: $g$-factor, linewidth $\Delta H_{pp}$ and abundances of the components of the total spectrum were evaluated.

Total concentrations and concentrations of paramagnetic centres responsible for the component lines were measured. Ultramarine was used as the reference for the concentration of paramagnetic centres. A ruby crystal, permanently placed in the resonance cavity, served as internal reference. The total concentration of the paramagnetic centres in the sample was calculated as:

$$N = n_u[(W_u A_u)/P_u] \cdot [P/(WAm)] \ , \quad (1)$$

where $n_u$ is the number of paramagnetic centres in ultramarine, $W$ and $W_u$ are the receiver gains for the sample and ultramarine, $A$ and $A_u$ are the amplitudes of the ruby signal for the sample and ultramarine, $P$ and $P_u$ are the areas under the absorption curves for the sample and ultramarine, and $m$ is the mass of the sample. Double integration of the first-derivative EPR spectrum was performed to determine the area under the absorption curve. The concentrations of paramagnetic centres responsible for the component EPR lines were calculated from their percentages in the total spectrum. The influence of microwave power (20–0.5 dB) on the EPR spectra was analysed. The changes of the intensities of the EPR component lines of the heated (at 300 and 650°C) macerals with temperature from liquid-nitrogen to room temperature were measured.

## 3. Results and Discussion

### *3.1. Multicomponent Structure of EPR Spectra of Macerals*

Numerical analysis of lineshape of experimental EPR spectra indicates multicomponent structure of coal and its macerals [14, 24]. The EPR spectra of the studied coal are superposition of four lines: broad Gaussian, broad Lorentzian (1), and two narrow Lorentzian (2, 3) lines. The number of component lines depends upon the kind of maceral. The EPR spectra of exinite and vitrinite are superposition of two, broad and narrow, Lorentzian (1, 3) lines and one broad Gaussian line. For inertinite two types of paramagnetic centres with narrow (broader and narrower) Lorentzian (2, 3) lines were found.

The ranges of the EPR linewidths of the four groups of paramagnetic centres of the studied coal and macerals are: 0.78–0.85, 0.48–0.60, 0.34–0.36 and 0.14–0.20 mT for samples in air [14, 27]. Unpaired electrons of structures consisting of a few aromatic rings are responsible for the broad EPR signals (Gaussian and Lorentzian 1) [2–5, 14, 27]. Dipole-dipole interactions of unpaired electrons and unresolved hyperfine structure of interactions of unpaired electrons with neighbouring protons result in the high values of the linewidths [13, 14, 26, 27]. Unpaired electrons of multiring aromatic structures, mainly delocalized $\pi$ electrons with strong exchange interactions, are responsible for narrow lines (Lorentzian 2, 3) [13, 14, 26, 27].

The $g$-values of the four groups of paramagnetic centres [14, 27]: 2.0030–2.0031 (Gaussian), 2.0028–2.0029 (Lorentzian 1), 2.0028 (Lorentzian 2) and 2.0027–

2.0028 (Lorentzian 3) for samples in air, indicate existence of unpaired electrons on carbon atoms and rather low content of unpaired electrons localized on heteroatoms in the analysed coal and macerals [13, 14, 27].

The measurements of changes of the intensities of component lines of the EPR spectra of macerals with microwave power show their different microwave saturation behaviour [24]. The narrow EPR lines (Lorentzian 2, 3) of the macerals satu-

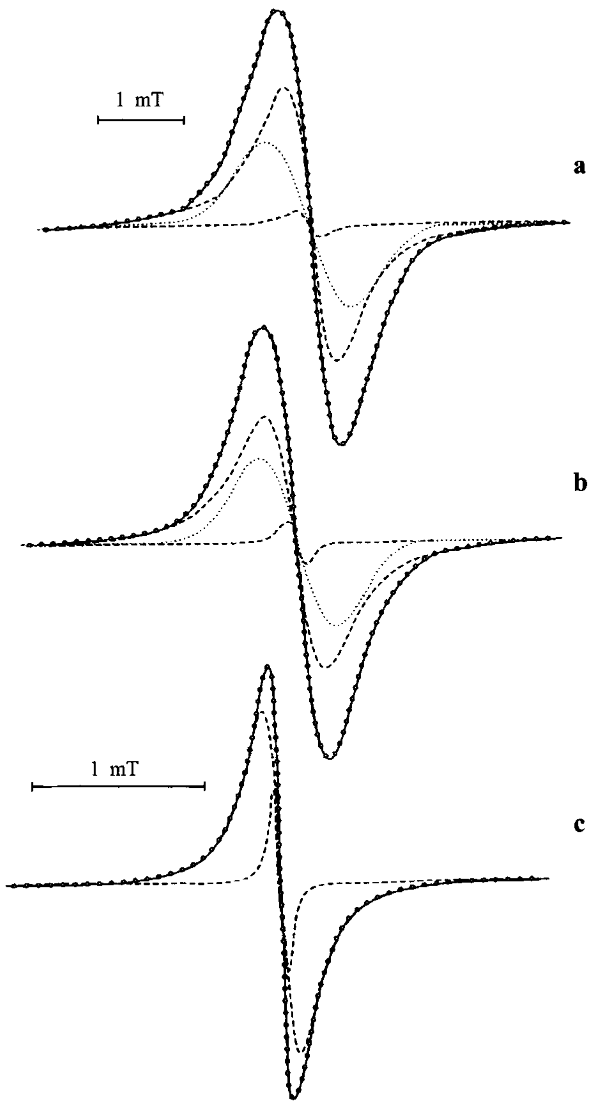


**Fig. 2.** EPR spectra of exinite (**a**), vitrinite (**b**) and inertinite (**c**) from durain for samples heated at 500°C. Experimental curve (open circles), theoretical approximation (solid line), Gaussian line (dotted line), Lorentzian line (dashed line).

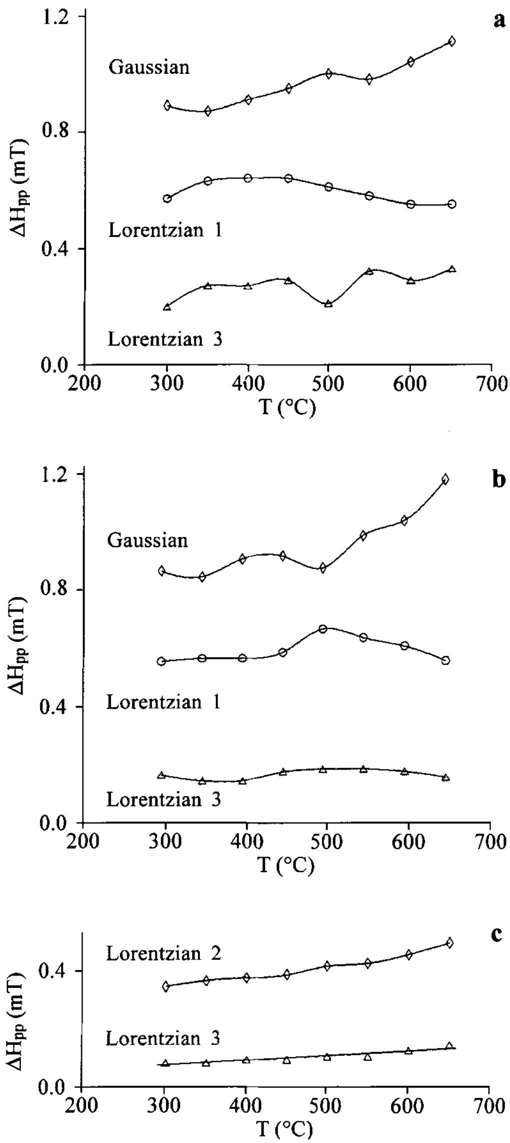


**Fig. 3.** **a** Changes in linewidths ($\Delta H_{pp}$) of the three EPR components of exinite from durain with temperature of heating [22]. **b** Changes in linewidths ($\Delta H_{pp}$) of the three EPR components of vitrinite from durain with temperature of heating. **c** Changes in linewidths ($\Delta H_{pp}$) of the two EPR components of inertinite from durain with temperature of heating.

rate at higher microwawe powers and unpaired electrons responsible for these lines reveal the lowest spin-lattice relaxation times. The decrease of spin-lattice relaxation time for unpaired electrons belonging to large aromatic structures was also confirmed by EPR and FTIR studies of coals with different carbon contents [4].

All paramagnetic centres of the studied macerals interact with paramagnetic atmospheric oxygen [27]. The changes in EPR parameters after evacuation of the samples were observed. The most active in interactions with oxygen are paramagnetic centres with the narrowest Lorentzian 3 lines. The narrowing of these lines after evacuation was recorded. Both decrease and increase of the concentrations of paramagnetic centres with narrow Lorentzian 3 lines were measured after removal of oxygen from the environment of the macerals. The breaking of weak "quasi-chemical" bonds between maceral and $O_2$ molecule is responsible for the increase of concentration in the evacuated samples. A so far unexplained decrease in concentration of paramagnetic centres after evacuation of samples probably results from changes in spin-lattice relaxation times of unpaired electrons in macerals due to interactions with oxygen molecules.

### *3.2. Thermal Decomposition of Macerals*

The influence of heating of macerals in the temperature range of 300–650°C on *g*-factor, linewidths and concentration of different groups of paramagnetic centres was determined. The number of different groups of paramagnetic centres remains constant during thermal decomposition of macerals. Three component lines were observed for the EPR spectra of exinite and vitrinite, and two-component EPR spectra were recorded for inertinite. For example, the total EPR spectra and their components for the in air samples of durain exinite, vitrinite and inertinite heated to 500°C are presented in Fig. 2. The *g*-values of unpaired electrons only slightly change during thermal decomposition of macerals. The changes of dipolar and exchange interactions of unpaired electrons in heated macerals lead to the broadening or narrowing of their EPR lines (Figs. 3–5, the data for samples in air).

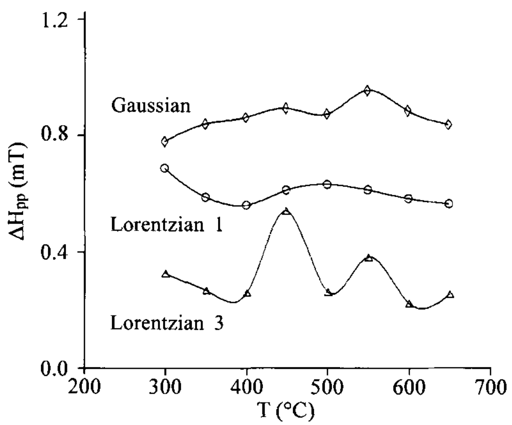


**Fig. 4.** Changes in linewidths ($\Delta H_{pp}$) of the three EPR components of vitrinite from vitrain with temperature of heating [21].

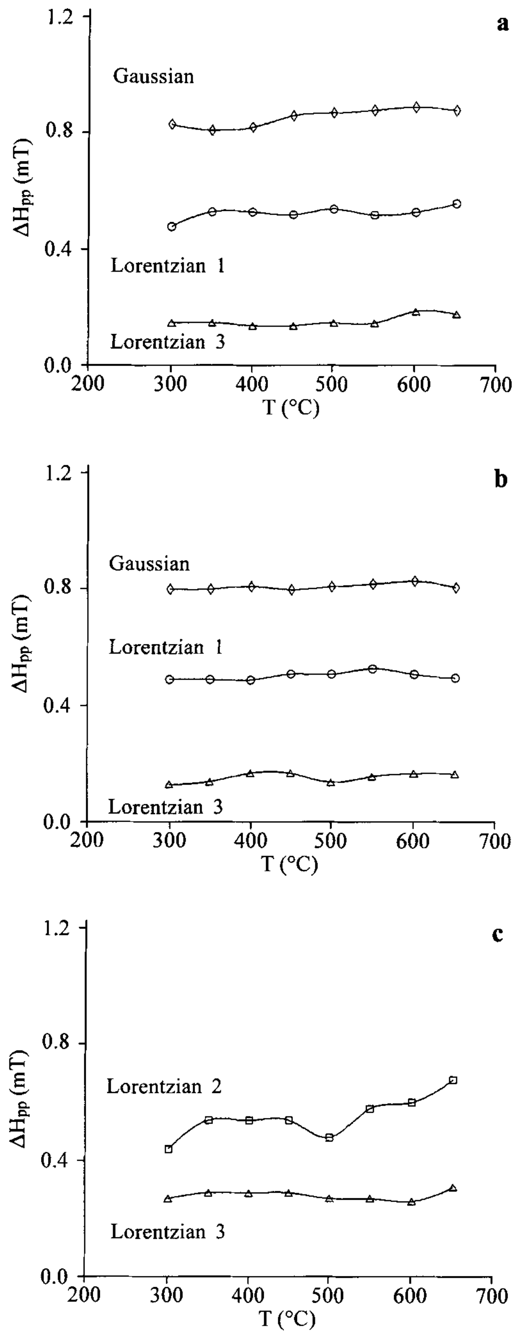


**Fig. 5.** **a** Changes in linewidths ($\Delta H_{pp}$) of the three EPR components of exinite from clarain with temperature of heating. **b** Changes in linewidths ($\Delta H_{pp}$) of the three EPR components of vitrinite from clarain with temperature of heating. **c** Changes in linewidths ($\Delta H_{pp}$) of the two EPR components of inertinite from clarain with temperature of heating [22].

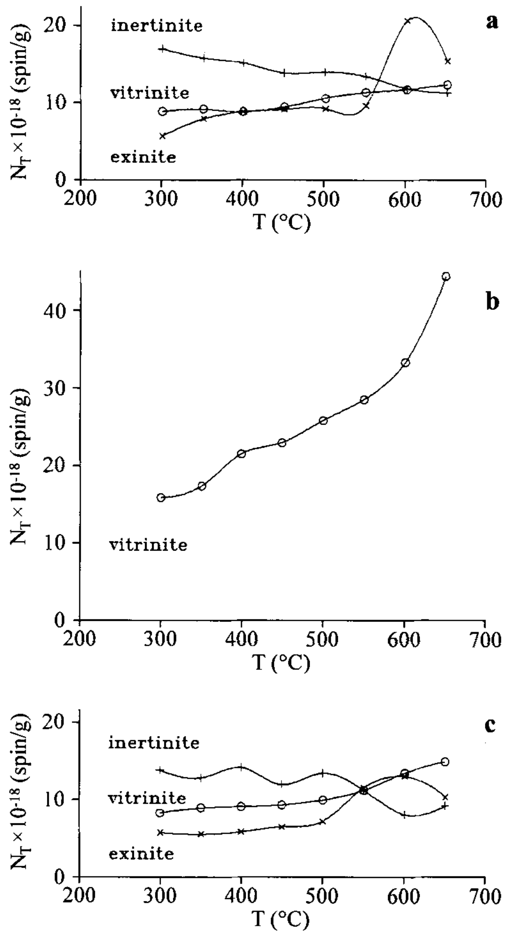


**Fig. 6.** **a** Changes in total concentration ($N_T$) of paramagnetic centres in macerals from durain with temperature of heating. **b** Changes in total concentration ($N_T$) of paramagnetic centres in vitrinite from vitrain with temperature of heating [21]. **c** Changes in total concentration ($N_T$) of paramagnetic centres in macerals from clarain with temperature of heating.

The considerable changes of the total concentration of paramagnetic centres of the studied macerals with temperature of heating above 500°C (Fig. 6, the data for samples in air), where the loss of mass of the heated samples is the highest (Fig. 1), was observed. During thermal decomposition paramagnetic centres are formed by cleavage of covalent bonds between elements of condensed structures, and they are stabilized by hydrogen atom transfer, mainly from the aliphatic part of the sample. Condensation of larger fragments of multiring structures is accompanied by hydrogen evolution, formation of paramagnetic centres and quenching of these centres during the final phase of heating. Formation of paramagnetic centres predominates in heated vitrinite

(Fig. 6a–c). Total concentration of paramagnetic centres in exinite increases at 500–600°C and decreases at 600–650°C (Fig. 6a, c). Because of appearance of condensation effect total concentration of paramagnetic centres in inertinite decreases above 500°C (Fig. 6a, c). The discussed increase or decrease of concentration is caused mainly by changes of concentration of paramagnetic centres responsible for broad Lorentzian 1 line of exinite and vitrinite (Fig. 7a, b, Fig. 8, Fig. 9a, b; the data for samples in air). The other EPR line components only insignificantly change with temperature of heating (Figs. 7–9).

Thermal decomposition of macerals influences the saturation behaviour of the component lines of their EPR spectra [21–23]. EPR lines of macerals heated at higher temperatures saturate at relatively higher microwave powers. The lowering of the spin-lattice relaxation time of unpaired electrons in heated macerals is responsible for this effect.

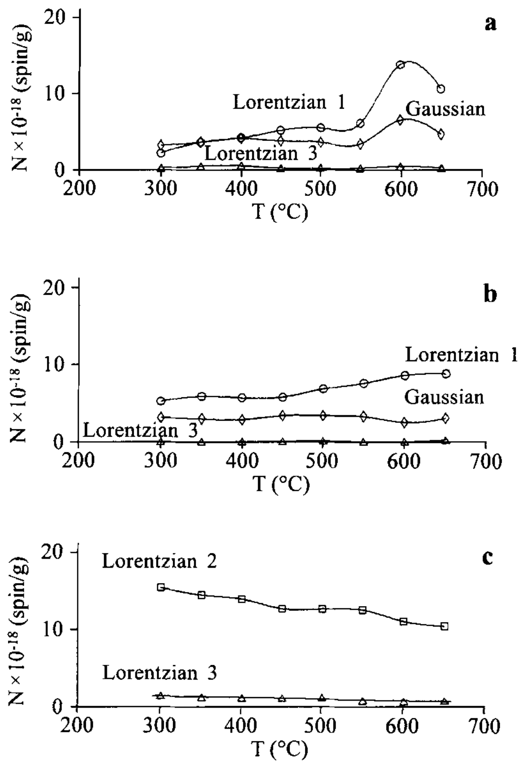


**Fig. 7.** **a** Changes in concentrations (*N*) of three types of paramagnetic centres with Gaussian and Lorentzian (1, 3) lines in exinite from durain with temperature of heating [22]. **b** Changes in concentrations (*N*) of three types of paramagnetic centres with Gaussian and Lorentzian (1, 3) lines in vitrinite from durain with temperature of heating. **c** Changes in concentrations (*N*) of two types of paramagnetic centres with Lorentzian (2, 3) lines in inertinite from durain with temperature of heating.

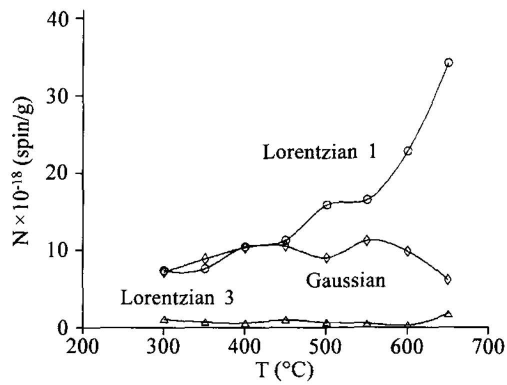


**Fig. 8.** Changes in concentrations (*N*) of three types of paramagnetic centres with Gaussian and Lorentzian (1, 3) lines in vitrinite from vitrain with temperature of heating [21].

We have checked the view about independent progress of reactions in macerals during heating of coal [28]. Comparative EPR analysis of both high-purity maceral samples and petrographically complex coal samples during heating at 300–650°C distinctly indicates reactions between paramagnetic centres of exinite, vitrinite and inertinite during thermal decomposition of coal [23].

### *3.3. Thermally Excited Multiplet States in Coal*

In an earlier study we have found that in bituminous coal thermally excited triplet states exist [29]. There is a controversy between our measurements and the results obtained by Rothenberger *et al.* [30]. The mentioned authors have stated that no excited triplet states exist in bituminous coal. In the work of Smirnova *et al.* [31] a suggestion was made of existence of quadruplet states with $S = 3/2$. We have decided to investigate the temperature dependence of line intensity on macerals. The measurements of line intensity for the individual components of the EPR spectra for each maceral were carried out in the range between the temperature of liquid nitrogen and room temperature. We have found that the broad Lorentzian line present in the EPR spectra of exinite and vitrinite is responsible for the temperature dependence of integral line intensity, which does not fulfil the Curie law. This proves the existence of thermally excited multiplet states in coal.

## 4. Conclusions

Multicomponent structure of the EPR spectra indicates existence of four different groups of paramagnetic centres in the investigated macerals. Three groups of paramagnetic centres with broad Gaussian, broad Lorentzian (1) and narrow Lorentzian (3) lines exist in exinite and vitrinite. Two narrow Lorentzian (2, 3)

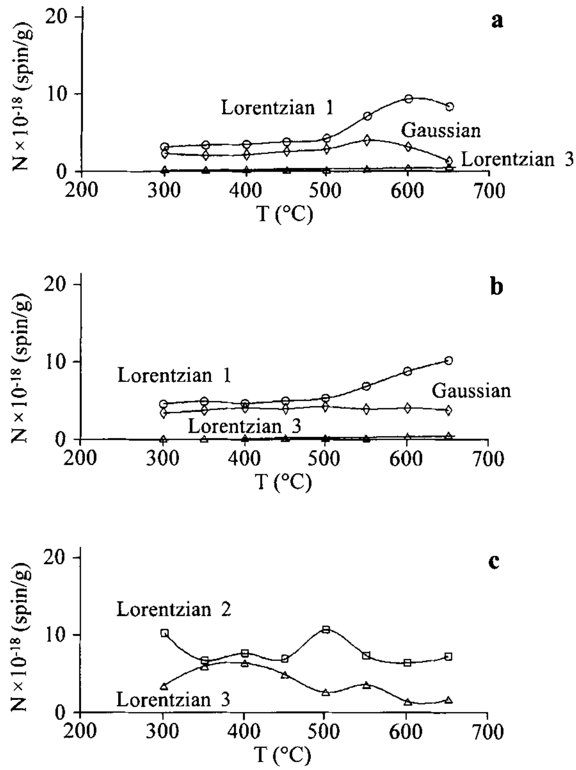


**Fig. 9.** **a** Changes in concentrations (*N*) of three types of paramagnetic centres with Gaussian and Lorentzian (1, 3) lines in exinite from clarain with temperature of heating. **b** Changes in concentrations (*N*) of three types of paramagnetic centres with Gaussian and Lorentzian (1, 3) lines in vitrinite from clarain with temperature of heating. **c** Changes in concentrations (*N*) of two types of paramagnetic centres with Lorentzian (2, 3) lines in inertinite from clarain with temperature of heating [22].

lines were observed for inertinite. Paramagnetic centres of the individual groups differ in dipolar and exchange interactions, and spin-lattice relaxation time.

Thermal decomposition of macerals changes concentration of paramagnetic centres in macerals and their physical behaviour. Paramagnetic centres with the broad Lorentzian (1) lines are the most active ones in the thermal decomposition. Paramagnetic centres of exinite, vitrinite and inertininite react during heating of coal.

The existence of thermally excited multiplet states in heated exinite and vitrinite was proved. Paramagnetic centres of inertinite obey the Curie law.

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