

Application of the 2D Heterospectral Correlation Spectroscopy (^{13}C NMR \times EPR) in Brazilian Soils from Reclaimed Oil Shale Mining Area

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1. Introduction

Currently, the world population is mobilized looking for methods to minimize the accumulation of wastes without stopping the industrial development. A major concern has manifested in the agriculture sector, through the reuse of wastes from agricultural and industrial activity as soil conditioners [1, 2] since the environment risks assessment caused by their use are respected and known.

The soil organic matter (SOM) is considered essential in the development of soil biological activity, stabilizing the structure and capturing organic and inorganic pollutants, been the main focus of several studies [3, 4]. In the SOM studies, the treatment of soil samples with solutions of HF to extract silicates and concentrate the organic material improves the quality of EPR and ^{13}C NMR spectra [5]. During the reaction, the F^- ion is released to break links such Al-O, Fe-O and Si-O, forming soluble complexes. Residual paramagnetic metals can interfere in spectroscopic analysis, but also can serve as paramagnetic probes [6]. In this sense, methods of correlation between EPR and ^{13}C NMR spectral data are of great importance in the SOM study and its interaction with paramagnetic metal ions remaining in the soil samples after extraction [6].

Reserves of oil shale occur in several Brazilian regions, an impressive outcrop occurs in the region of São Mateus do Sul city (PR, Brazil) where the Oil Shale Industrialization Unit from PETROBRAS / SIX is located. The recovery of the degraded areas after the oil shale mining is made arranging the mining by-products in a systematical form, followed by the recovering of the area with clay and soil. This recovery soil relief process has being made for more than 30 years [7].

In this sense, the objective of this work was to study the nature of interactions between inorganic and organic structures of the SOM from Brazilian oil shale mining reclaimed soils through the 2D heterospectral correlation spectroscopy (^{13}C NMR \times EPR).

2. Materials and Methods

The studied samples were collected at different depths from the soil profile in the Petrobras mining area, city of São Mateus do Sul (PR), Brazil. It was collected six samples from the mining reclaimed area and five samples from a native forest as reference soil samples.

For the study of SOM and its interaction with the paramagnetic metal ions, the treatment of the soil samples with 10% HF solution to extract silica composites and concentrate the organic material was applied [5]. After this HF treatment that improves the quality of the spectra, the EPR and ^{13}C NMR analysis were performed. The EPR spectra were recorded at room temperature (~ 300 K) and liquid N_2 (77 K), in a Bruker EMX micro spectrometer operating at X-band (9.5 GHz), using 100 kHz of modulation frequency.

For the ^{13}C NMR spectra it was carried out experiments of Cross Polarization with Magic Angle Spinning (CPMAS), using the Variable Amplitude Cross Polarization (VACP) technique. It was used the Total Spinning Sidebands Suppression (TOSS) technique of four pulses to eliminate the rotational sidebands. The experiments of Chemical Shift Anisotropy (CSA) filter and quantification of aromatic structures were performed using a five-pulse CSA dephasing filter, and four-pulse TOSS [8].

The EPR and ^{13}C NMR spectra analysis were correlated using 2D heterospectral correlation, which provides information about the interaction between organic groups and paramagnetic ions of SOM.

3. Results and Discussion

In the EPR spectra it was observed: a) signals of rhombic Fe^{3+} ($g \sim 4.3$ and 8.9); b) broad line attributed to associated Fe^{3+} ions (concentrated domains) in $g \sim 2.0$ and c) narrow line attributed to the organic free radicals (OFR) in $g \sim 2.0$ [9]. Because the soils are classified as Oxisoil type, hence the presence of intense signal of Fe^{3+} ions.

By the ^{13}C NMR spectra, evidence of typical SOM chemical groups was observed as: alkyl, N-alkyl (aminoacids) and methoxyl (lignin), O-alkyl and di-O-alkyl (cellulose), aryl, O-aryl, carboxyl and amide [6,8]. In the samples of reclaimed areas, especially those collected at deeper layers, there was a predominance of hydrophobic groups (alkyl and aryl), probably

from fossil organic matter. These samples are composed specially by oil shale by-products. During this restoration process, soil and oil shale by-products can be in contact among others, which may explain the presence of fossil organic matter in the soils collected in the deeper reclaimed area.

Correlating the two techniques, EPR and ^{13}C NMR, (Fig. 1), it was obtained: a) positive correlation between hydrophilic groups (mainly uronic acids) and associated Fe^{3+} ions in rhombic structures, and b) negative correlation of the same hydrophilic groups with the OFR signal, indicating the involvement of these hydrophilic groups in the complex formation of Fe^{3+} ions which probably lead to the suppression of the OFR signs [6,8]. Alternatively, the lower content of OFR and higher content of hydrophilic compounds may be associated to a more labile SOM (less humified).

The data correlating in the OFR region ($\Delta B = 5$ mT) showed at least two different paramagnetic species: a) the spin density is probably located upon O atoms ($g = 2.0042$) and, b) the density is probably upon C atoms ($g = 2.0029$). The specie with higher g was negatively correlated with hydrophilic groups (higher content of Fe^{3+}), reinforcing the hypothesis of paramagnetic suppression [6, 8].

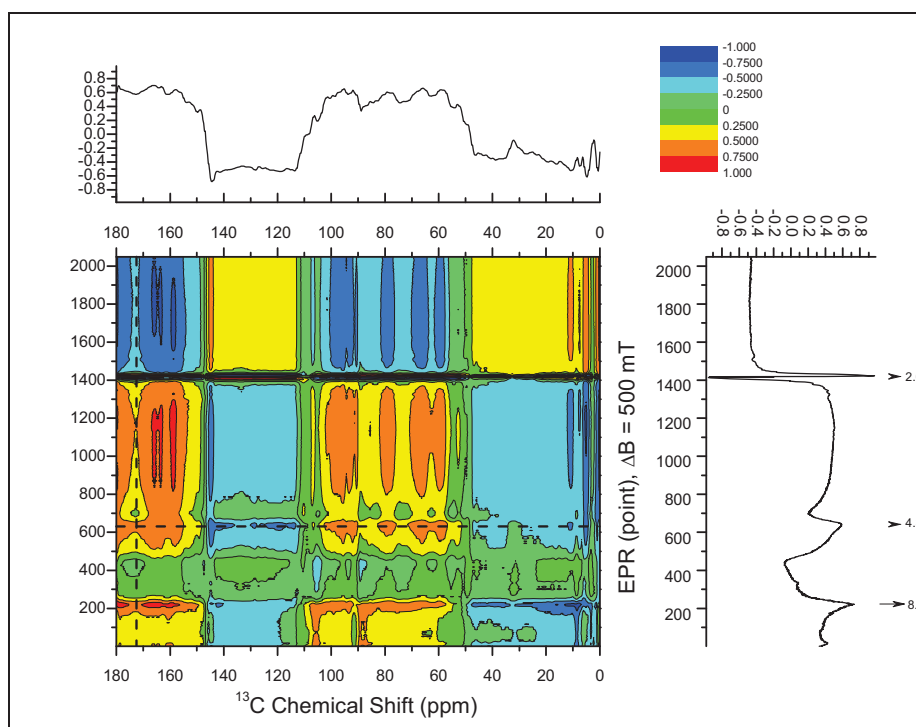


Figure 1: Correlation between the data of EPR and ^{13}C NMR spectra of the soil samples

4. Conclusion

It was observed that the soils from the native area were composed specially of more labile SOM structures, probably related to the degradation of plant structures. And the soils from the reclaimed area showed structures probably related to the fossilized organic matter. The hydrophobic aromatic structures were positively correlated with the OFR associated with C atoms. The OFR signal associated with O atoms was correlated inversely with the concentration of Fe^{3+} ions and with hydrophilic organic structures, indicating the involvement of these hydrophilic structures in the formation of complexes with these metal ions. This suggests the suppression of the OFR signal by paramagnetic ions.

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