Thesis Summary

THE CHEMICAL AND ANALYTICAL CONTROL OF HUMIC ACIDS IN NATURAL PRODUCTS

Scientific Coordinator,
Prof. PhD Alexandru Popescu

PhD student,
Irina Daniela Nicolaescu

The PhD thesis entitled “The Chemical and Analytical Control of Humic Acids in Natural Products" is a detailed description of humic substances existing in the natural products (coal, peat, compost).

The paper consists in 135 pages, divided into two distinct parts (the theoretical and experimental part), and contains 54 figures, 6 tables and 113 references.

The theoretical part consists in 41 pages, which present a comprehensive scientific documentation in this research field conducted in recent years.

The class of natural compounds, generically called "The group of humic acids" is of a particular interest, because they form a link between vegetal substances and coals. The humic acids are widespread in nature and they originate in the organic waste from plants and living organisms, which are under a complex biochemical metamorphosis. The high concentration of humic acids in humic coals is primarily due to their concentration during the genetic material’s incarbonization process under strict anaerobic conditions for a long period of time. The complexity and the diversity of these natural products are closely related to the origin of the genetic material and appearance conditions, thus the humic acids characterization required first of all their separation and purification.

The documentary part contains an introduction to the knowledge of humic substances, their classification being described in a well-synthesized scientific mode. There are reviewed the main types of humic substances whose classification is given in detail. The theoretical part includes information based on bibliographic researches on humic substances focusing on the formation of humic substances in soil, their structure, and the use of humic acids and a study of the quantitative determination of humic substances. According to these studies the conclusion is that each of these methods can give only a part of the information and only all the results from all methods can provide a complete picture of the phenomena and properties.

The theoretical part consists of 90 bibliographic references.

The original part of this paper begins with collecting and characterizing the samples, followed by obtaining and purification of humic acids in natural products, and also their analysis by classical methods and modern instrumental methods. The experimental part continues with a study concerning the influence of humic substances on the soil’s antioxidant activity and its cationic exchange capacity, in order to exploit the experimental results in obtaining organo-mineral fertilizers based on lignite.

The humic acids are macromolecular, heterocyclic, condensed substances, with different degree of polymerization and multiple, complex organic functions.

From the chemical point of view, the humic acids are characterized by aromatic and polycondensate nuclei and by their acid character due to the carboxyl groups, phenolic hydroxyl and metoxydic groups.

I have collected the samples according to the standard instructions referring to collecting and processing the average representative samples.

For the experimental measurements, I have used coal samples under 50 μ grains.

I have obtained the humic acids from natural products using the solvent extraction. During this study, I have noticed that the formic acid is not recommended to be used for soils with high content of Co, Fe, Al and other inorganic components soluble in formic acid, because they pollute the extracted organic matter from which they cannot be separated, the extraction efficiency being about 53%. When I have used chelating agents for the extraction of humic acids, the results were below expectations and satisfactory only for certain types of soil.

In the case of the extraction with an alkaline solution, it occurs the oxidative degradation reaction of certain constituents under stirring conditions and long extraction time. The more alkaline the solution is and the longer the period of extraction is, the chemical changes of the other components are greater so thus the error of the acids determination is higher because of the contamination.

The optimum pH is 7, because at this pH the changes of aluminosilicates, so common in alkaline extraction, are completely removed.

I have achieved the purification of extracted humic acids by common purification methods as: extraction, precipitation, and filtration.

The analyses performed in this study show that the lignite with a high content of xiloidic component is poor in humic acids extractable in an alkaline medium. Since the exploitable lignite layers contain variable amounts of xilitic coal, in order to process them to obtain the organo-mineral fertilizers with high content in humic acids, I recommend these layers which are poor in this petrographic component taking into account their properties (increased resistance to crushing, lower specific weight, lower friction coefficient, etc.).

The chromatographic analysis performed on a Finnigan-Surveyor chromatograph show that the standard potassium humates as well as the extracted ones present a single peak with a maximum intensity of about 1.667 minutes, which is similar to that registered observed at the standard potassium humates (Fig. 31).

The spectrophotometric analysis performed on a Carry 50 spectrophotometer show that the standard humic acids and experimentally obtained humic acids present UV-VIS spectra with maximum absorption at the same wavelength ranging between 200 and 400 nm (Fig. 33 and 34).

Next, I have used the thermal analysis in order to characterize the lignite from Rovinari coalmine. For this purpose, during the experiments, I have used a Diamond TG / DTA derivatograph from Perkin-Elmer Instruments, and experimental data were processed using Pyris software. I have analyzed the influence of various compounds (aromatics, organic acids, alkanes, ketone, heterocyclic) on humic acids' (from lignite) thermal stability, as well as their oxidative decomposition kinetics.

The lignite from Rovinari contains about 11-12 % humidity water. Up to 105 ^{o}C (Fig. 36), the thermograms indicate the loss of the absorbed water (the first endothermic peak in the DTA and DSC curves), followed by the elimination of the structural water up to 110 ^{o}C. The rest of about 2-3 % of water is due to the organic functions. The pyrolysis of the carboxylic groups and small catenae (known as “volatiles”) takes place between 200-320 ^{o}C. The start of the carbon’s burning can be noticed from the differential caloric and thermal curves, undergoing from 320 to 550 ^{o}C. Beyond a 500 ^{o}C temperature, the DTG curve indicates two exothermic reactions, corresponding to the oxidative decomposition of resins and metal-sulphide materials. A residue of about 30.5 % remains after the non-isothermal analyze at about 650 ^{o}C.

I have further studied the thermoanalytical curves of the non-isothermal decomposition of ammonium humates extracted from the lignite originated in the Rovinari mine (Fig. 37) as well as the potassium humates in the same conditions. Comparing the thermal decomposition of the ammonium humates and the decomposition process of potassium humates, it results that the latest is much simple due to the absence of the ammonia groups (Fig. 38).

The thermoanalytical curves of the coaly matter separated from the potassium humates (Fig. 40) preserve the characteristics of raw lignite but it concentrate a higher amount of oxides and carbonates, which endothermically react (620-700 ^{o}C). Due to the smaller content in organic compounds of the coaly matter, the obtained residue (58 %) is higher than that one obtained after the thermal treatment of Rovinari lignite (30.5 %).

The inorganic part separated from the coaly matter also named sterile showed DTA and DSC exothermic peaks (Fig. 41) which are a characteristic of the thermal behavior of the organic compounds and coke. The weight of the residue after the calcination of the sterile (43 %) should be higher than the one resulting after burning the coal matter (52 %). The explanation of this behavior in that, inside the sterile aggregations, the coal was bounded and it can be released only at temperatures higher than 600 °C function of a higher pressure and grain constitution.

Afterwards I have experimentally studied the influence of humic substances on the antioxidant activity of the soil in order to obtain organo-mineral fertilizers based on lignite. Together with the reserve of the nutritive material in soil, the soil antioxidantive capacity is another property of humus which is very important during the process of the vegetative activity of crops. The antioxidative activity of the humus is given by the presence of the polyphenolic substances in soil, as a result of a chemical, biochemical and enzimatical degradation.

The pyrogalol and galic acid from the composition of humus, together with phenolic products belonging to C_6-C_1 group compounds resulted from the enzymatic degradation of the lignine, have a significant importance to the antioxidative activity of the humus.

Based on the spectrophotometric analysis, the calculated value of the antioxidative activity is 27%, given only by the water soluble substances.

These substances are formed by humic acids (fulvic acids), intermediate decomposition substances of the organic wastes participating in humic acids formation, aromatic compounds such as poliphenols (3,57%), resulted from lignine’s degradation and aminoacids derived from the proteic substances hydrolysis process.

I have observed that the pyrogalol and galic acid have a significant importance in the antioxidative activity of the humic matter.

During this studies I have observed that the humic substances (humic acids and fulvic acids) participate in redox and radicalic processes, and their antioxidative capacity can be used to evaluate these properties. I have also observed that this antioxidative capacity is a quantitative property of the efficiency of the humic substances to inactivate the reactive species of oxygen.

Based on the experimental results obtained during the study, I could exploit them in order to obtain organo-mineral fertilizers based on lignite. This has been realized at S.C. Chimenerg S.A. Craiova on a pilot station (Fig. 53) using the wet method and the dry method.

The production of the organo-mineral fertilizers by using the wet method was mainly as the dry one, taking into account that the lignite mass must remain sufficiently fluid in the reactor. The fluidity must be maintained by a constant stirring process, using a low concentration phosphoric acid and using wet coal, and, if necessary, by adding water.