Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 433 (2005) 77–82

thermochimica acta

www.elsevier.com/locate/tca

Influence of alkaline extraction on the characteristics of humic substances in Brazilian soils

André Henrique Rosa[a,*], Luciana Camargo de Oliveira[b], Iramaia Corrêa Bellin[b], Julio Cesar Rocha[b], Luciane Pimenta Cruz Romão[c], Newton Luiz Dias Filho[d]

[a] *Department of Environmental Engineering, São Paulo State University (UNESP), 18087-180 Sorocaba, SP, Brazil*
[b] *Department of Analytical Chemistry, Institute of Chemistry (UNESP), 14800-900 Araraquara, SP, Brazil*
[c] *Department of Chemistry, Federal University of Sergipe (UFS), 49100-000 Aracajú, SE, Brazil*
[d] *Department of Physical and Chemistry, University of the São Paulo State (UNESP), 15385-000 Ilha Solteira, SP, Brazil*

Received 1 October 2004; received in revised form 31 January 2005; accepted 2 February 2005
Available online 8 March 2005

Abstract

An investigation was made of the influence of alkaline extraction on the characteristics of humic substances extracted from Brazilian soil samples. Humic substances (HS) from seven different soils samples collected in Brazil were extracted using the procedure recommended by the International Humic Substances Society (IHSS). Soils, HS and humins were characterized by thermogravimetry and differential thermal analysis. About 8 mg of each material (soil, HS and humin) were placed in a platinum crucible and heated continuously from 20 to 750 °C at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ in an atmosphere of synthetic air ($100\,\mathrm{ml\,min^{-1}}$). A thermal analysis revealed a difference between the content and structural characteristics of organic matter present in HS and humin fractions in relation to their soils. The results indicated that alkaline extraction alters the characteristics of humic substances during the extraction process, underlining the importance of developing methodologies and analytical procedures that allow organic matter in soils to be studied without extracting it.

Keywords: Humic substances; Humin; Brazilian soils; Extraction; Thermogravimetry and differential thermal analysis

1. Introduction

The main fraction of organic matter contained in soils, peat, sediment and natural water consists of humic substances (HS), which are comprised of a complex mixture of physically heterogeneous substances, with different sizes and molecular weights and a large number of functional groups containing oxygen [1,2]. Due to their structural characteristics, HS control several physical and chemical properties of soil, e.g., stability of aggregates, buffering capacity, sorption of hydrophobic organic compounds and transport, bioavailability and complexation of metals present in the environment [3,4]. Investigations of the structure of humic substances (HS) are important because their structure governs the properties and reactions of these materials in the environment. For decades, the chemical structure of humic substances has been investigated using several techniques, particularly infrared and UV-visible spectroscopy, nuclear magnetic resonance, spin electron resonance, fluorescence and PY–CG–MS to gain a better understanding of the structure of humic matter [5–8].

The structural, chemical and functional properties of HS can be studied in detail in the free state, i.e., when free of inorganic components [4,9]. Therefore, several procedures have been proposed in the literature for the extraction of HS using alkaline solvents, chelating agents, organic solvents and aqueous saline solutions [10–12]. Alkaline solvents were the earliest reagents used for extracting HS and remain the most efficient and widely used [8–10]. The International Humic

---

[*] Corresponding author. Tel.: +55 15 32383414; fax: +55 15 32282466.
E-mail address: ahrosa@sorocaba.unesp.br (A.H. Rosa).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.02.001

Substances Society (IHSS) recommends a standard procedure based on a 4 h treatment with 0.1 mol L^{-1} NaOH at room temperature in an N_2 atmosphere [10,13,14]. After this period of alkaline treatment, the soluble alkali extract is operationally defined as a humic substance (HS) and can be separated from the residue (humin), which is composed of organic matter linked with mineral phase [6]. However, this procedure has been criticized in the literature because the alkaline extraction can promote some structural alterations in the HS, in particular, auto-oxidation and other chemical modifications, including the breakdown of humic macromolecules and condensation of amino-carbonyls [9,10].

In the field of environmental chemistry it is very important that the results obtained in laboratories can be used to shed light on environmental processes. Thus, it is crucial that HS not be altered during their extraction. In this work, differential thermal analysis and thermogravimetry were used to study the influence of alkaline extraction on the characteristics of organic matter present in seven different soil samples collected in Brazil. Differential thermal analysis (DTA) and thermogravimetry were chosen for this study because they are interesting techniques for studies involving the characterization of organic matter in soils, and because they allow for analyses of original samples without chemical treatment, which is an indispensable characteristic for the type of study proposed here.

2. Experimental

2.1. Chemicals and reagents

Diluted acids and bases required to isolate the HS were prepared by diluting 30% hydrochloric acid solution (p.a. Merck AG, Darmstadt/Germany) and sodium hydroxide monohydrate (p.a. Merck AG), respectively, with high purity water (Millipore-Q system, Millipore GmbH, Eschborn/Germany).

2.2. Collection of samples

The soil samples were collected from soil surfaces (0–20 cm) in different regions of Brazil. The collection sites are depicted in Fig. 1. The dried soil samples were ground and passed through a 2 mm sieve. The fertility of the soil samples (Ca, K, Mg, P, S, CEC) was characterized using the methodology described by Raij et al. [15]. The atomic ratios of C/N were calculated after determining the carbon and nitrogen using a Perkin-Elmer 240 – C elemental analyzer. Table 1 lists the physico-chemical characteristics of the soil samples.

2.3. Humic substances and humin extraction

The humic substances were extracted according to the procedure recommended by [7,10–12]. Five grams of the sieved material were extracted with a volume of 0.1 mol L^{-1} HCl solution equal to 10 times the weight of the sample. The pH of the solution was adjusted between 1 and 2 using 1.0 mol L^{-1} HCl solution. The soil/HCl mixture was shaken for 1 h and the suspension was allowed to settle. The mixture was then centrifuged at $1478 \times g$ for 10 min, and the supernatant separated from the sediment. The latter was neutralized with 1.0 mol L^{-1} NaOH solution at pH 7.0 and a volume of 0.1 mol L^{-1} NaOH solution equal to 10 times the weight of the sample. The mixture was shaken for 4 h under a nitrogen atmosphere and then allowed to settle overnight, after which the soluble supernatant (HS) was separated from the insoluble sediment (humin) by centrifugation at $1478 \times g$ for 10 min. HS and humin were dried at 55 °C in an oven equipped with an exhaust system until they reached a constant weight. The percentage of extracted HS was calculated in relation to the mass of soil subjected to extraction (5.0 g), while the percentage of humin was calculated by subtracting the percentage of HS from 100% (Table 2).

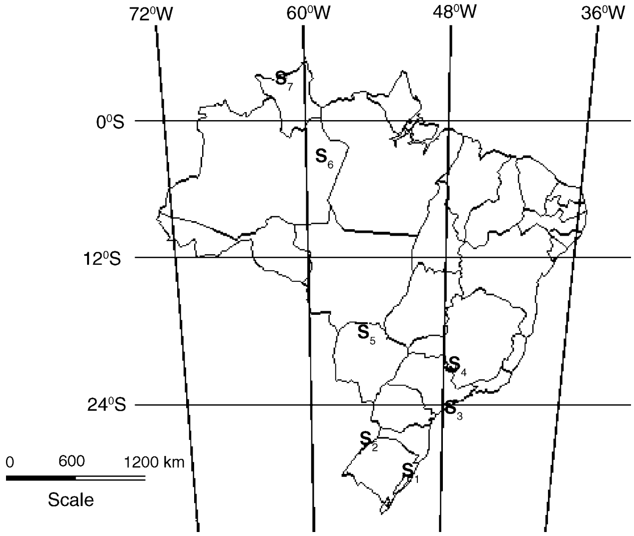

Fig. 1. Soil sample collection sites in Brazil (S_1: Santa Maria (RS), S_2: Bento Gonçalves (RS), S_3: Cananéia (SP), S_4: Ribeirão Preto (SP), S_5: Campo Grande (MS), S_6: Manaus (AM) and S_7: Boa Vista (RO)).

2.4. Differential thermal analysis (DTA) and thermogravimetry (TG)

The intact soil, extracted HS and humin (residue from the alkaline extraction of the HS) samples were ground with a mortar and pestle and sieved through a 70 mesh (0.2 mm) sieve to homogenize them and increase their surface area.

For the DTA and TG analysis, about 8 mg of each material (soil, HS and humin) were placed in a platinum crucible and heated continuously from 20 to 750 °C at a heating rate of 10 °C min^{-1} in a synthetic air atmosphere (100 ml min^{-1}). The DTA and TG curves were recorded simultaneous using a TA Instruments STA-2960 Simultaneous DTA–TGA