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## Phase separation methodology for physicochemical studies of soils

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**Abstract.** A detailed study of a soil in every country is of a paramount importance, because it determines an entire economic strategy. The mineralogical properties of soils have been studied in the world for more than 100 years by various characterization techniques, X-ray diffraction being the most prominent. The main difficulty in most of employed techniques is the dominance of the majority phases in the response or the measured signal from the sample that becloud minority phases preventing their identification. The application of methods of phases' separation would provide the possibility to discern minority phases in soils. This work presents a phase separation method that employs a combination of two phenomena based on principles of fluid dynamics: flotation and sedimentation. Different characterization methods were used to analyse the produced soil samples. The methodology employed for separation of phases allowed the complete separation of clay phase from heavier mineral phases. This result makes it possible to discern minority mineral phases of soils that are difficult to detect. A more accurate determination of the mineralogical composition of a soil becomes feasible.

### 1. Introduction

Soils are composed of a mixture of numerous minerals, amorphous substances and organic complexes intimately associated in a variety of compositions in different areas of the planet. Inasmuch as the production of our food and the quality of our environment are related to the rational use of a soil, it is very important to thoroughly study its chemical mineralogy. Due to the great structural diversity, the soils' compositions are rarely identified and quantified in totality.

The X-ray diffraction is the standard technique for the identification of minerals. It allows reliable identification and quantification of mineral phases, especially when combined with such techniques as X-ray fluorescence and thermogravimetry. Over the last few years the transmission electron microscopy (TEM) has been playing an increasingly important role in this regard [1]. Even with the separation of phases, the identification of experimental diffraction peaks using the available databases does not allow a reliable identification of minerals. The use of computer modeling programs for powder X-ray diffraction patterns (e.g. via Rietveld method) increases the chances of identifying the different phases in a soil. To date, no attempts to combine the experimental procedures of phase separation of soils with computational methods of analysis of the phases within separated fractions were taken.



The separation of a series of mineral species, as singly as possible, prior to the application of various techniques for a soil's analysis, would be the key part to the identification of the exact nature of mineral soils. The methods for effective separation of phases that preserve their physical and chemical characteristics are rare and, in many cases, inefficient for detailed structural elucidation of mineral components.

Therefore, the aim of this study was to develop a methodology for a separation of mineralogical phases that enhances the capabilities of the techniques for a quantitative characterization of soils.

## 2. Experimental

### 2.1. Preparation of soil samples and phases separation

Soil samples from an Acrisol were collected on soil surface (0-20 cm depth) in the county of Mojú in the State of Pará in Brazil. This kind of soil is most representative of this region. Soil samples were initially crumbled and cleaned out of any unwanted wastes. The combination of two methods was used for the separation of phases: the flotation process coupled with the principles of fluid dynamics of particles. The terminal settling velocity,  $v$ , of an isolated particle with equivalent spherical diameter  $D_p$  moved by a constant force in the fluid of density  $\rho_f$  and viscosity  $\mu_f$  is given by the empirical equation [2].

$$v = \frac{\mu_f}{D_p \cdot \rho_f} \cdot \left[ \left( k_1 \frac{C_D Re^2}{24} \right)^{-1.20} + \left( \frac{C_D Re^2}{k_2} \right)^{-0.60} \right]^{-0.83} \quad (1)$$

where  $C_D$  is the particle's drag coefficient,  $Re$  is the Reynolds number,  $k_1$  and  $k_2$  are coefficients dependent on a particle's shape. This equation allows estimating optimal speed for phase separation in a solvent with a given density. Upon this established methodology, it was possible to separate, with the help of a magnetic stirrer, the studied soil sample in 9 compositionally different solid fractions.

### 2.2. Instrumentation

The chemical composition of the sample was determined by X-ray fluorescence using the S4-Pioneer spectrometer from Bruker-AXS. The bottom fraction (fraction number 9) has been chosen then, in which one might expect the highest probability of dense minerals in order to elucidate the identity of these mineralogical phases.

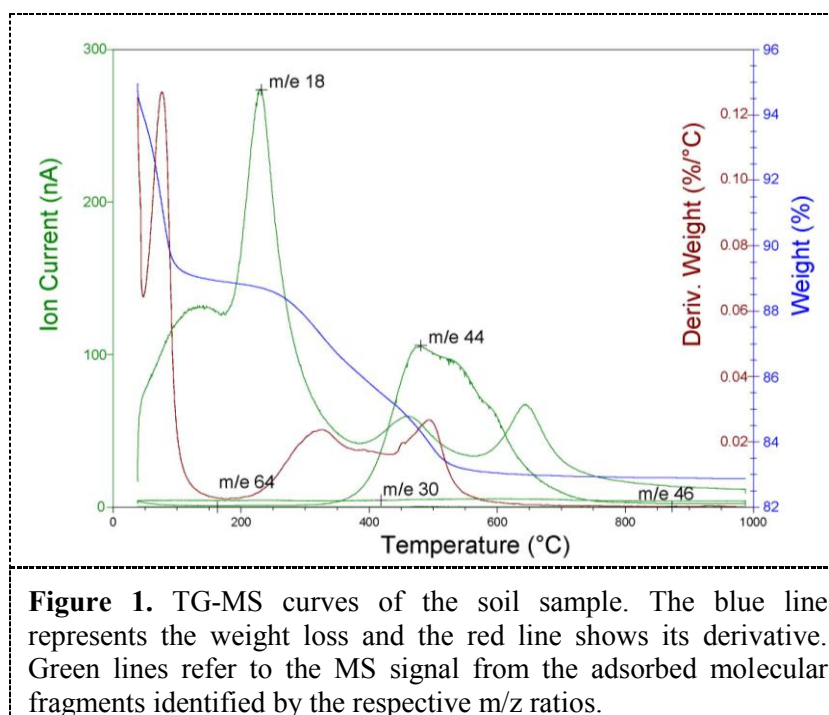
The thermogravimetry (TG) coupled to mass spectrometry (MS) allowed the separation and identification of the released gases. Thermogravimetric analysis (TGA) data were recorded using a Universal V4.5 TA instrument coupled to a mass spectrometer.

X-ray diffraction analysis has been carried out in order to determine the crystalline phases present in the studied compounds. The powder diffraction patterns from fractions were collected on D8 Focus diffractometer from Bruker-AXS using Cu-K $\alpha$  radiation (33 keV and 50 mA, Ni filter) with a  $2\theta$  step of  $0.02^\circ$  in the measurement  $2\theta$  range from  $2^\circ$  to  $80^\circ$ . The resulting patterns were fitted to the theoretical spectra using Rietveld structural refinement.

## 3. Results and discussion

The results of TG-MS are shown in Figure 1. The use of this technique in materials science and specifically in mineralogy has a long history. The analyzes of the integral soil samples performed herein are uncommon, mainly because of a soil being a mixture of mineral and organic matter, in which the organic component may mask characteristic peaks of strongly exothermic reactions of decomposition of certain minerals. The observed total mass loss of approximately 12% was partially (about 9%) attributed to dehydration and partially (~3%) originated from carbon compounds. A small percentage of the fragment ions with mass-to-charge ratio ( $m/z$ ) of 46 indicates an eventual traces of nitrogen compounds. No ions having  $m/z=64$  were observed, which otherwise would indicate the possible presence of sulfur compounds.

By looking at  $m/z=18$  related to the desorbed water, one can see four regions of intense mass loss. The first region between  $30^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  is related to the loss of adsorbed water in the soil. The temperature interval between  $200^{\circ}\text{C}$  and  $360^{\circ}\text{C}$  can be assigned to dehydroxylation of inorganic compounds [3]. The region between  $380^{\circ}\text{C}$  and  $560^{\circ}\text{C}$  is a characteristic region of dehydroxylation of clays of kaolinite type [4], whereas the highest temperature region is related to the decomposition of hydroxy-silicates.



**Figure 1.** TG-MS curves of the soil sample. The blue line represents the weight loss and the red line shows its derivative. Green lines refer to the MS signal from the adsorbed molecular fragments identified by the respective  $m/z$  ratios.

The ions having  $m/z=44$ , related to the desorption of  $\text{CO}_2$ , would be produced from decomposition of carbon composites. The thermal decomposition that took place below  $500^{\circ}\text{C}$  can be associated with a burning of organic carbon produced by living tissues, sap, microbes, fungi and animals. While a more stable carbon with the decomposition temperature range above  $500^{\circ}\text{C}$  would be of mineral origin. There is a big variety of complex chemical compounds of carbon; many have not been yet classified [5].

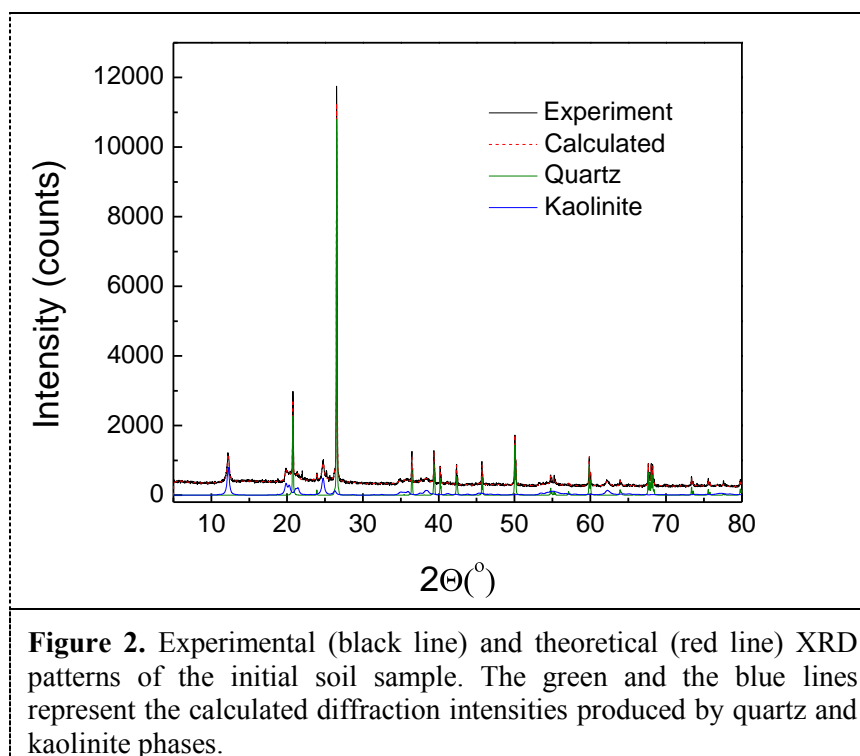
Ions with  $m/z=46$  and  $64$ , related to  $\text{NO}_2$ , and  $\text{SO}_2$  fragments, respectively, were also examined. A small amount of nitrogen dioxide indicating nitrated compounds was detected while no MS signal was obtained for sulfur dioxide. This result does not discard the presence of sulfur-based compounds in the samples. Most probably, these substances are in very low quantities making their detection difficult.

Table 1 shows the results of XRF analysis. The results are semi-quantitative, showing only the relative amount of elements detected in the fraction 9 of the soil. This analysis when combined with XRD and TG-MS techniques, aims to assist in the elucidation of the possible phases.

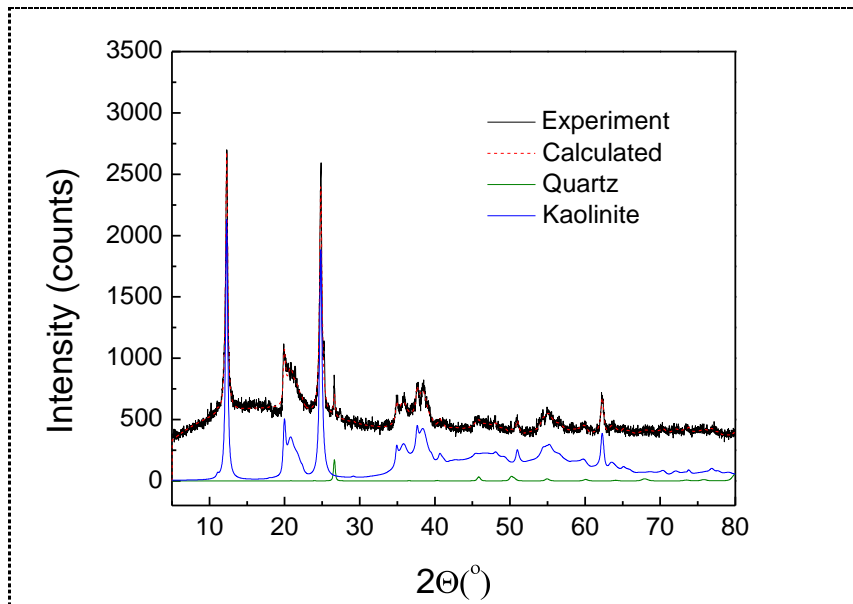
Figure 2 shows the XRD pattern of the original soil sample, without separation. Two major phases, clay (61%) and quartz (39%) were observed, it being not possible to clearly distinguish any other mineral phase. The crystallographic phase of clay corresponds to kaolinite ( $\text{H}_4\text{Al}_2\text{SiO}_9$ ).

**Table 1.** XRF analysis of the fraction 9 of the soil sample. Concentration of the elements is given in atomic %.

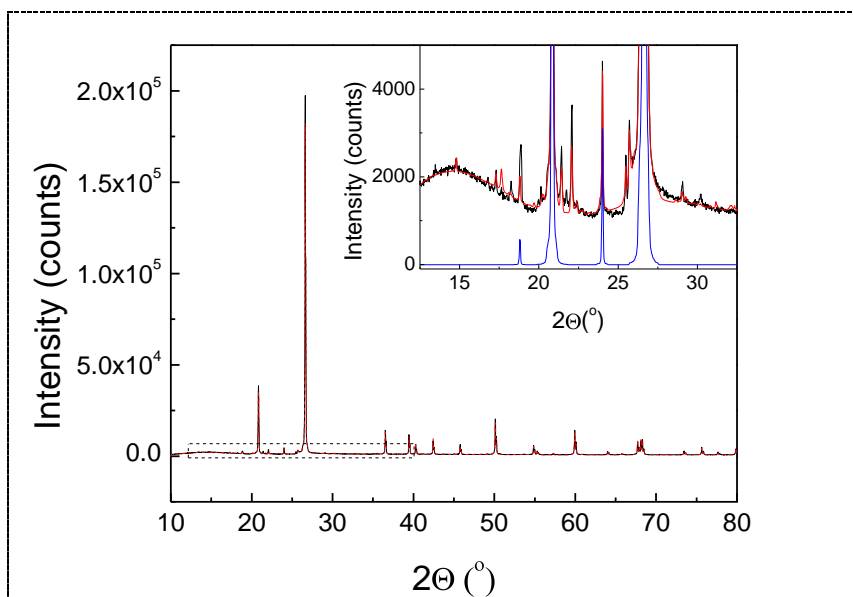
Element	Concent.	Element	Concent.	Element	Concent.	Element	Concent.
<b>Si</b>	48.2	<b>Au</b>	0.3	<b>Ru</b>	0.1	<b>Ba</b>	0.03
<b>Al</b>	29.8	<b>Zr</b>	0.2	<b>Cl</b>	0.1	<b>Mg</b>	0.02
<b>Fe</b>	12.5	<b>P</b>	0.2	<b>In</b>	0.08	<b>K</b>	0.01
<b>Ti</b>	6.5	<b>S</b>	0.2	<b>Bi</b>	0.07	<b>Pr</b>	0.01
<b>Ca</b>	0.4	<b>Ni</b>	0.1	<b>Zn</b>	0.05	<b>Th</b>	0.002
<b>Cr</b>	0.3	<b>Mn</b>	0.1	<b>Se</b>	0.05		
<b>Cd</b>	0.3	<b>U</b>	0.1	<b>La</b>	0.04		



The methodology for phases separation applied to the studied soil sample allowed us to separate it in nine fractions. Figure 3 shows the XRD pattern of the fraction 4, which composition consisted of more than 99% of clay phase (kaolinite) with a small amount of quartz (<1%), whereas the last fraction (number 9) shown in Figure 4 exhibits the complete withdrawal of the clay phase. Although the quartz phase dominates the composition of this fraction (75%), other mineral phases present in the soil become visible in the diffractograms, thus allowing their identification. To this end, we applied the Rietveld method which is based on the variation of instrumental, structural and microstructural parameters inserted into mathematical models that describe in the best possible way the whole experimental diffraction pattern. The excellent fit to the latter was obtained by modeling the majority phases.



**Figure 3.** Experimental (black line) and theoretical (red line) XRD patterns of the fraction 4. The green and the blue lines represent the calculated diffraction intensities produced by quartz and kaolinite phases.



**Figure 4.** Experimental (black line) and calculated (red line) XRD patterns of the fraction 9. The inset shows the zoomed region of the diffraction pattern. The blue line in the inset denotes the calculated diffraction intensities produced by quartz. The diffraction intensities of the visible small peaks were calculated assuming the structural models of minority phases presented in the table 2.

Table 2 shows the result of possible phases present in the bottom fraction (fraction 9), applying this methodology of analysis. Nevertheless, some observed reflections remained not indexed with the supposed phases. This fact may indicate the presence of other minority phases in the bottom fraction.

**Table 2.** List of possible crystallographic phases found in the bottom fraction

Phase	Chemical Formula
Quartz	SiO <sub>2</sub>
Pseudobrookite	MgO <sub>5</sub> Ti <sub>2</sub>
Olivine	Fe <sub>1.249</sub> Mg <sub>0.749</sub> O <sub>4</sub> Si
Kalsilite	KAlSiO <sub>4</sub>
Berlinite	AlO <sub>4</sub> P
Prehnite	Ca <sub>2</sub> Al(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Gold	Au
Ferrocyanide	Fe(CN) <sub>2</sub>
Lithium Aluminosilicate	Li <sub>0.25</sub> Al <sub>0.25</sub> O <sub>2</sub> Si <sub>0.75</sub>
Lithium Aluminosilicate	Li <sub>0.33</sub> Al <sub>0.33</sub> O <sub>2</sub> Si <sub>0.67</sub>

#### 4. Conclusions

The methodology employed for separation of phases allowed the complete separation of clay phase from heavier mineral phases. This result makes it possible to discern minority mineral phases of soils that are hard or impossible to detect without an efficient separation. As a consequence, a more accurate determination of the mineralogical composition of a soil becomes feasible.

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