Determination of different Fe oxides using EDXRF

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1. Introduction

Throughout time and weather conditions in several kinds of soils, it is found different crystal phases of Fe oxides, such as the minerals Goethite ($FeO(OH)$), Ferrihydrite ($Fe_5HO_84H_2O$), Hematite (Fe_2O_3) e Magnetite (Fe_3O_4), which are of great interest to the study of soil genesis. For characterization of these phases several techniques are applied, including X-Ray Diffraction (XRD), Raman Spectroscopy, as well as many other techniques of analytical chemistry that are based in exchange, extraction and measure of cations[1], becoming complex and expensive. This work had as objective the usage of the spectroscopy technique EDXRF (Energy Dispersive X-Ray Fluorescence)[2], associated with PCA (Principal Component Analysis) statistical analysis in a methodology that was able to group samples with different chemical phases of Fe in soils and evaluate which one would be in higher concentration[3]. It was made X-Ray Fluorescence analyses on 10 different soil samples, and from the characteristics photopeaks and incoherent scattering obtained in each one of them, was able to group samples with similar phases of Fe oxides. Throughout this method it is possible to reduce the amount of processes during characterization, increasing analysis speed and minimal sample preparation.

X-ray fluorescence is a multi-elemental, non-destructive analytical technique used to obtain qualitative and quantitative information on the elemental composition of samples. This methodology is based on the production and detection of characteristic X-rays emitted by the constituent elements of the sample when it is irradiated with electrons, protons, X-rays or gamma rays at appropriate energies[2]. Iron oxides are the second largest group of minerals present in soils in the tropical region of the planet, making this a region of great fertility, especially in the so-called Latossolos, typical of the south and southeast of Brazil[4]. Present in soils are important pieces for the characterization of its provenance (since its genesis) and its composition, in minerals the main Fe oxides are present as Goethite ($FeO(OH)$), Ferrihydrite ($Fe_5HO_84H_2O$), Hematite (Fe_2O_3) and Magnetite (Fe_3O_4), and may be present in more than one crystalline phase in a given soil and may be transformed from one oxide to another according to the weathering.

2. Methodology

Ten soil samples of different oxide concentrations and provenances were analyzed (samples: 111, 114, 133, 135, 144, 203, 206 and 209), as well as pure samples (100%) of different iron oxides (Goetita, Hematita, Ferrihidrita e Magnetita) and mixed samples (from 15% to 50%) of these oxides (A1, A2, A3, A4 and A5). The following oxides were observed: Goethite (FeO(OH)), Ferrihydrite (Fe$_5$HO$_8$4H$_2$O), Hematite (Fe$_2$O$_3$), Magnetite (Fe$_3$O$_4$) and Maghemite (γFe$_2$O$_3$). The soil samples (0.12022 g) were placed on appropriate x-Ray FunnellShape sample cups (Chemlplex Co.) with a polypropylene thin film of 5μm thick; the samples were grounded to about 125 μm and the spectra were obtained by a benchtop commercial EDX720 spectrometer, Shimadzu Co. with a rhodium tube, 3 mm collimator, in two different channels ranging from 0-20 keV and from 0-40 keV, with 200 s per sample. The samples were also analyzed by a homemade Portable X Ray Fluorescence spectrometer with a Pu-238 source, a X-123 Complete X-Ray Spectrometer (Amptek Inc., USA) and 100 s (acquisition live time). Seventeen elements were identified through these spectra, among which the most concentrated were Fe, Al, Si and Ti. From the spectral regions of the Fe and excitation source scattering peaks, statistical PCA principal component analyses were performed for the clustering of the different crystalline phases of the respective oxides, using the Matlab R2021a software.

3. Results and Discussion

For the soil samples were also identified other elements such Al, Si and Ti. Fig. 1 shows a superposition spectra of all the samples soils where can be observed the slighty difference in the Compton scattering peaks from the excitation source (Rh_KaC and RhKb-C) which are responsible for the discrimination of the different oxides. Through the ratios between iron photopeaks and scattering photopeaks, from the excitation source, it became possible to group and differentiate the oxides present in the analyzed soil samples. Fig. 2 shows the results from PCA analysis, where can be observed the clustering of the different Fe oxides.
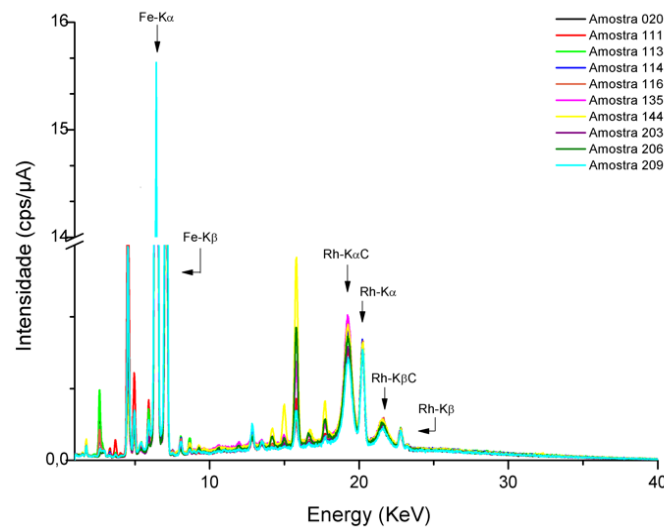

Figure 1: Superposition spectra of all the samples soils where can be observed the slighty difference in the Compton scattering peaks from the excitation source of Rhodium (Rh_KaC and RhKb-C).
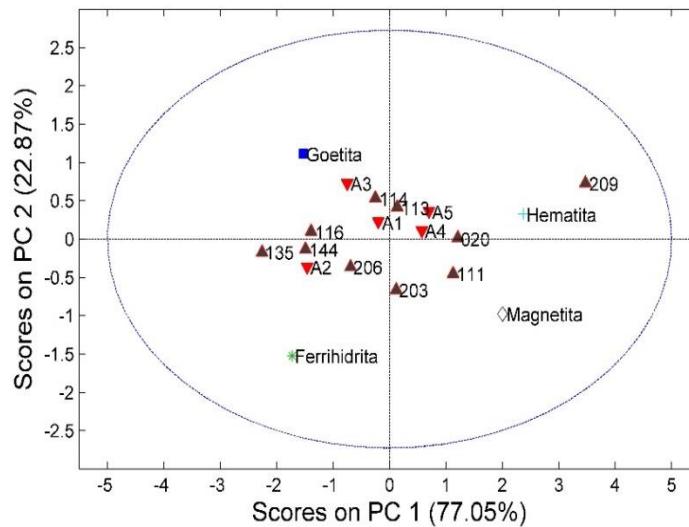
Figure 2: Scores of Principal Components Analysis where can be observed the clustering of the soils samples with respect to iron oxides.

4. Conclusions

The data obtained by the EDXRF equipment provided satisfactory spectra for the samples analyzed, when taking into account the minimal preparation that was performed on the samples, the measurement time, and the non-destruction of the object of analysis. And it was possible with the proposed methodology to obtain the clustering of the different phases of iron oxides present in soil samples, based on the fact that the scattering process of the excitation source, is mainly due to the presence of light elements, as oxygen and carbon present in the structure of the oxides, opening the possibility of future studies to improve the methodology.

Acknowledgements

References

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