Radiation Physics and Chemistry 81 (2012) 1796–1803

Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Qualitative soil mineral analysis by EDXRF, XRD and AAS probes

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HIGHLIGHTS

- ► Qualitative soil minerals analysis by EDXRF, AAS and XRD methods.
- ► There is a requirement of other means and methods due to inadequacy of XRD.
- ► Principal component analysis (PCA) provides an idea of minerals present in soil.
- ► Trace elements complexes can be determined by AAS probe.
- ► EDXRF, AAS and XRD, in combination, enable successful soil minerals study.

ARTICLE INFO

Article history:
Received 27 December 2011
Accepted 5 July 2012
Available online 22 August 2012

Keywords:
EDXRF
Principal component analysis (PCA)
Minerals
X-ray diffraction (XRD)
AAS

ABSTRACT

Soil minerals study is vital in terms of investigating the major soil forming compounds and to find out the fate of minor and trace elements, essential for the soil–plant interaction purpose. X-ray diffraction (XRD) has been a popular technique to search out the phases for different types of samples. For the soil samples, however, employing XRD is not so straightforward due to many practical problems. In the current approach, principal component analysis (PCA) has been used to have an idea of the minerals present, in qualitative manner, in the soil under study. PCA was used on the elemental concentrations data of 17 elements, determined by the energy dispersive X-ray fluorescence (EDXRF) technique. XRD analysis of soil samples has been done also to identify the minerals of major elements. Some prior treatments, like removal of silica by polytetrafluoroethylene (PTFE) slurry and grinding with alcohol, were given to samples to overcome the peak overlapping problems and to attain fine particle size which is important to minimize micro-absorption corrections, to give reproducible peak intensities and to minimize preferred orientation. A 2θ step of 0.05°/min and a longer dwell time than normal were used to reduce interferences from background noise and to increase the counting statistics. Finally, the sequential extraction procedure for metal speciation study has been applied on soil samples. Atomic absorption spectroscopy (AAS) was used to find the concentrations of metal fractions bound to various forms. Applying all the three probes, the minerals in the soils can be studied and identified, successfully.

1. Introduction

Qualitative soil phase analysis is a non-trivial endeavor that is important to observe the main soil forming compounds, complex formation mechanism between different elements and to find toxic compounds in the soil. However, performing X-ray diffraction (XRD) with soil samples is not so simple because of many complexities like variable chemical and structural compositions of soil minerals, including interstratification with swelling interlayers and various defects that may cause large differences in the XRD reflection intensities between different species of the same mineral. Furthermore, the thickness of diffracting domains, particle size, particle-size distribution, and the sample weight or thickness in the holder, sample preparation, XRD instrument alignment, and data collection procedures may all contribute significantly to the problem (Aparício and Ferrell Jr., 2001). Above all, the complexes of minor elements yield broad low-intensity XRD peaks, and these peaks often overlap with high-intensity peaks from silica, thereby making identification and quantitative determination difficult. Some of the minerals like calcite and dolomite do not cause problems (Emig and Smith, 1989) but quartz does interfere. Pickard et al. (1985) lists some of the interferences of quartz with other minerals. The XRD peaks of most of the minerals including kaolinite, maghemite, muscovite, sillimanite etc., which are among the main soil forming components, overlap with the strongest peak and other peaks of quartz.

In the present study, three probes i.e. energy dispersive X-ray fluorescence (EDXRF), atomic absorption spectroscopy (AAS) and X-ray diffraction (XRD) have been used simultaneously to overcome the problems mentioned above. The EDXRF technique,

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0969-806X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2012.07.002

in combination with the PCA method, is helpful. Multielemental analysis, by EDXRF technique, of soil is easier than phase analysis, by XRD, due to the difficulties mentioned above. The superiority of the EDXRF technique is due to less cumbersome sample preparation. Soil samples, prepared in the form of pellets, can be analyzed directly without any chemical procedure or preconcentration method. The method provides reliable results for both major and trace elements, of $Z \geq 13$, up to ppm level concentration. Earlier, researchers have used EDXRF with PCA for many different purposes (Yu et al., 2002; Jorgensen et al., 2005; Zerrouqi et al., 2008).

PCA is a dimension reduction technique in which the data reduction is performed by transforming the data into orthogonal components that are linear combinations of the original variables (Jolliffe, 1986). Typically, PCA is used to reduce the dimensionality of a data set, while retaining as much of the original information as possible. This reduction is achieved by transforming the original set of variables into a new smaller set of variables, the principal components, which are uncorrelated and the first few principal components (PCs) retain most of the variation present in the original variables.

XRD study of soil samples has been done to find the phases in the sample. First, silica is removed from the sample following a slightly modified procedure of Dobrowolski (2001), who used the method to avoid the matrix effect caused by silica in determination of selenium in soil samples by graphite-furnace atomic-absorption spectrometry. To identify the peaks of different phases, the 'MATCH!' software installed with ICDD database was used. Manually, it is a tough task to identify all the peaks in XRD pattern of a complex material like soil. The software compares each diffraction pattern in the reference pattern database, ICDD PDF-2, to the pattern of unknown sample. It calculates a numerical value indicating the degree of agreement, the so called figure-of-merit (FoM) and the entries with the high value of FoM are the ones that are more likely to be present in the sample.

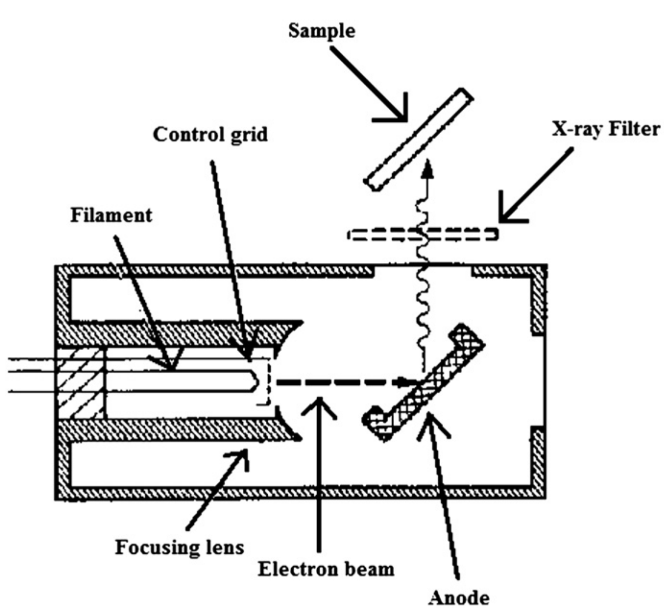

Fig. 1. Direct filtered X-ray tube excitation system.

Again, to know the fractions of trace metals bound in different forms, the AAS technique was used. The XRD technique was found incapable of identifying the minor minerals in samples. The samples for the AAS study were prepared by a five-step extraction scheme that can distinguish the metal fraction bound to ion-exchange form and carbonate, Fe–Mn oxides, organic matter, humic compounds and sulphide.

2. Methodology

2.1. EDXRF set-up

All measurements were carried out under vacuum, using a Jordan Valley EX-3600 EDXRF spectrometer. This consists of an X-ray tube with a Rh anode as the source of X-rays with a 50 V, 1 mA power supply, a Si(Li) detector with a resolution of 143 eV at 5.9 keV Mn X-ray and a 10-sample turret that enables mounting and analyzing 10 samples at a time. The direct excitation mode (Fig. 1) was used to irradiate the samples by the X-rays emitted from the anode. In this mode, a primary X-ray beam filter can be used to modify the spectrum from the X-ray tube that is finally used to excite the elements in the sample. The concentrations of 17 elements, namely Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, S, Rb, Sr and Pb, were measured with the technique obtaining the maximum and minimum concentrations for Si and Cu, respectively. The built-in ExWin software was used for the quantitative analysis.

To optimize the EDXRF sensitivities for the wide range of elements of interest, three different combinations of EDXRF parameters (including voltage and current; Table 1) were employed for different elements for each soil sample. The X-ray filters were used for particular line energies to reduce the relevant background intensities.

2.2. Experimental site and soil taxonomy

The soil samples were collected from an agricultural field of G.B. Pant University of Agriculture and Technology, Pantnagar, lying in the tarai region of Uttarakhand, India. The soil of this particular region of tarai area has been classified as Mollisols. The experimental soil has subgroup—Aquic hapludoll, Family—Fine Loamy and series—Silty Clay Loam. Mollisols occur in regions of high soil fertility and fair-to-adequate rainfall so that they probably comprise the world's most productive agricultural soil. These soils are found in grassland areas and have a relatively rich, dark-colored surface zone as a result of the organic matter being added from the grass. The fertile nature of these soils makes them excellent media for growing grain crops.

2.3. Sample collection and preparation

A total of 24 samples have been collected randomly in a 1 ha field and coded as S1, S2, …, S24. The samples were air-dried, homogenized and sieved properly before making the pellets for

Table 1
Combinations of the parameters and X-ray filters used in the EDXRF setup to find the different elements.

Elements	Voltage (kV)	Current (μA)	Filter	Preset time (s)	Range (keV)	Atmosphere
Mg, Al, Si, K, Ca, S	6	75	Nil	600	10	Vacuum
Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn	14	300	Titanium (Ti)	600	10	
As, Se, Br, Rb, Sr, Pb	23	150	Iron (Fe)	600	10	