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X-ray spectrometry and X-ray microtomography techniques for soil and geological samples analysis

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ABSTRACT

A particular subject of X-ray fluorescence analysis is its application in studies of the multielemental sample of composition in a wide range of concentrations, samples with different matrices, also inhomogeneous ones and those characterized with different grain size. Typical examples of these kinds of samples are soil or geological samples for which XRF elemental analysis may be difficult due to XRF disturbing effects. In this paper the WDXRF technique was applied in elemental analysis concerning different soil and geological samples (therapeutic mud, floral soil, brown soil, sandy soil, calcium aluminum cement). The sample morphology was analyzed using X-ray microtomography technique. The paper discusses the differences between the composition of samples, the influence of procedures with respect to the preparation of samples as regards their morphology and, finally, a quantitative analysis. The results of the studies were statistically tested (one-way ANOVA and correlation coefficients). For lead concentration determination in samples of sandy soil and cement-like matrix, the WDXRF spectrometer calibration was performed. The elemental analysis of the samples was complemented with knowledge of chemical composition obtained by X-ray powder diffraction.

1. Introduction

The well-known X-ray spectrometry (XRF) technique [1–5] allows fast and accurate simultaneous analysis of many elements. It is routinely used in different applications to study the elemental composition of the samples [6–9]. A particularly, often this technique is used in studies of the multielemental sample of the composition in a wide range of concentrations, samples with different matrices, also inhomogeneous ones and those characterized with different grain size. Typical examples of these kinds of samples are soil or geological matrix samples (soil, till, sand, sediment and mineral). The elemental and chemical analysis of soil and geological samples is applicable in many fields of science, e.g. in agriculture, biology or geography [6,7,9–11]. One of the main and often concidered topic of these analyses is an influence of environmental pollution on soil heavy metals concentration. The knowledge of the elemental composition of soil samples is also important in understanding of the processes of soil formation, soil erosion and in determining geochemical till properties. Thus it is also possible to compare the composition and morphology of different samples in the study of their origin and the reconstruction of their geohistory. In the quantitative description of the phenomena the chemical composition of the sample is also important.

Despite the many advantages, however, XRF technique has shortcomings, e.g. so-called matrix effects and particle-size effects to name a few [3,4]. These interfering effects, which can seriously constrain the accuracy of the qualitative and quantitative XRF analysis, are caused by variations in the fluorescence intensities of the excited elements due to the chemical composition and granulation of the sample. In general, disturbing effects can be classified as: interelement radiation, the matrix effects, particle-size effects (grain-size effects, granulation effects) and mineralogical effects [3,4]. These effects influence both the intensity of characteristic X-ray and X-ray scattering radiation which mainly determine the continuous background observed in the measured X-ray spectrum. The scattered radiation may disturb the analysis, especially when a low concentration is determined. Weak signals of the characteristics radiation can be obscured by a strong background due to scattered radiation. Selecting optimum measurement conditions for X-

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ray fluorescence determination of a particular element in a given material requires information concerning the chemical composition and the expected concentration ranges of all sample constituents in all analyzed samples.

In a typical XRF sample preparation procedure, the analyzed material is crushed, ground (with different milling time) and formed as pellet (using different pressure). Sometimes different wax binders are used in the pellet formation process. The appropriate sample preparation procedure can reduce the disturbing effects.

The aim of the presented study was the analysis of the soil and geological samples with different matrices using the wavelength dispersive X-ray fluorescence technique (WDXRF) [3]. The samples had different elemental composition, grain sizes and different material packing. The main motivation of the undertaken research topic was the improvement of the qualitative and quantitative analysis of the materials with a particular kind of matter, namely, the soil and geological materials, and study of the influence of the preparation procedure on sample morphology and next on the reduction of XRF disturbing effects. The WDXRF elemental analysis was complemented with chemical composition analysis using the XRPD technique [12]. The morphology of each sample, especially sample grain size, was characterized in the micrometers scale using X-ray microtomography technique [13]. The obtained results of the analysis of the soil and geological samples were interpreted in the context of influence of the sample matrix on the elemental quantitative analysis. Additionally, some practical aspects of this analysis were discussed. The measurements were done with the WDXRF spectrometer – AXIOS (Panalytical) [14], X-ray diffractometer X'Pert (Panalytical) [15] and X-ray microtomograph SkyScan 1172 [16]. The first part of the paper describes the samples and the preparation procedure. Next, the experimental devices and measurement conditions are discussed. A further part of the work concentrates on the obtained results and discussion. The section conclusion summarizes WDXRF, XRPD and X-ray microtomography studies of soil and geological samples. The results obtained can be used to improve the accuracy and reliability of the XRF measurements.

2. Sample description and preparation procedure

2.1. Sample description

Soil and geological samples which were analyzed in presented studies have been chosen taking into account their different matrices, it was namely: peloid (therapeutic mud), floral soil, brown soil, sandy soil and calcium aluminium cement samples.

Peloid in form of mud or clay is used in balneotherapy and therapeutic bathing. Is used in the treatment of rheumatic diseases, gynecological diseases and certain diseases of the internal organs. Laboratory processed mud is a raw material for the production of various kinds of medicines and cosmetics. The samples of peloid analyzed under the presented studies came from a Polish health resort *Solec Zdrój* located in the south-central part of Poland.

Floral soil samples were commercially available different soil samples standard used in the cultivation of potted plants, while samples of brown soil (main type of soil in Poland) came from a leafy forest from southern Poland.

Sandy soil was a test sample of Worldwide Open Proficiency Test for X-ray Fluorescence Laboratories PTXRFIAEA10 [17] organized by the IAEA Nuclear Science and Instrumentation Laboratory in Seibersdorf, Austria. Sandy soil material, prepared and tested by an external independent laboratory, was as a powdered, homogenized, and dried material distributed to laboratories in order to determine the mass fractions of chemical elements making up the sample according to their routine analytical procedures.

The last sample was calcium aluminium cement which is a hydraulic binder used for the concretes and prefabricated elements, in heating devices operating up to a temperature of 1600 °C, in a special industrial building, in building chemistry as a component of mortars, in mining and in individual reparation and installation works (stacks, ventilation, fireplaces). Such extensive use of calcium aluminium cement is possible due to its special properties, such as: a short bonding time, rapid increase in mechanical strength and resistance to aggressive sulfate, sea water, carbon oxide, methane, the ability to use under subzero temperatures (−10 °C). Typical chemical composition of this material is as follows: Al_2O_3 (minimum 40%), CaO (minimum 36%), SiO_2 (3–6%), Fe_2O_3 (8–12%) and mineralogical basic phase is calcium monoaluminate. Sandy soil and calcium aluminum cement samples, for which elemental composition was known, can be used in presented studies as a reference materials.

2.2. Sample preparation procedure

For the wavelength dispersive X-ray fluorescence analysis (WDXRF) the samples had to be prepared as a pellet. Prior to pellet formation, the samples analyzed in the presented studies (therapeutic mud, floral soil and brown soil samples) were dried and ground with the compact ball mill (MiniMill2) at the rotation speed 300 rpm and different grinding time t = 1, 2, 3 and 6 min. The sandy soil and calcium aluminium cement samples did not require grinding. Next, the ground samples of 5–10 g were formed to the pellet. Usually in pellet formation the pelletizing pressure was 100 kN but for brown soil sample milled for 6 min additional pressure of 150 kN and 200 kN was applied. In general, it was expected that proposed sample preparation will result with the reduction of grain-size effect appearing for soil and geological samples. Calcium aluminium cement samples were also prepared by adding to the sample a wax binder ($C_{18}H_{36}O_2N_2$) whose mass was from 1% to 7% of the sample mass. The aim of the above test was to check influence of the amount od added binder on the on the quantitative analysis of the studied geological samples. Next, the elemental composition of prepared pellets was analyzed using the WDXRF method.

2.3. Experiment

The WDXRF analysis was performed using the AXIOS spectrometer (Panalytical) equipped with an Rh-anode X-ray tube with maximum power of 2.4 kW. The wavelength dispersive system of the spectrometer used five crystals (LiF (200), Ge (111), PE (002), PX1 and LiF (220)), which were automatically selected during the measurements. The characteristic X-rays induced in the sample were diffracted on one of the crystals and measured by flow proportional counter for optimal detection of elements up to Fe or a scintillation detector for heavier elements. In order to cover the X-ray energy (wavelength) range of the interest it was necessary to perform 12 scans with different diffraction crystal-detector configurations. Energy resolution of the setup (10–50 eV) allows for unambiguous identification of element intensity even for very rich in elemental composition samples. The measurements were performed in vacuum. The quantitative analysis of the spectra was performed with the PANalytical analytical program Omnian [14]. The Omnian package is available for the standardless analysis of all types of samples. Omnian includes advanced algorithms designed to profile known limitations inherent to XRF and includes spectral interference. The *darkmatrix* correction provides better accuracy in cases where light elements such as C, H and O contribute to significant absorbance. In generally, corrections

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