



Application of sequential extraction procedure for speciation of some trace elements in sediments and dump materials (East Maritza Basin, Bulgaria)

Приложение на процедурата за селективно екстрахиране за изследване разпределението на елементи-примеси в седименти и насипищни материали (Източномаришки басейн, България)

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Introduction

Studies on the elements fractionation among the mineral phases in shales, mud rocks and clayey rocks are rarer because of the fine grain-size structure and difficulties to separate discrete mineral fractions. Microprobe analyses can give information about the main elements content only, and not about the forms of the elements presence – e.g. adsorbed, isomorphous or organic. Selective extraction or single extraction procedures can help in studies of such a kind of fine sediments, on one hand. It could help also to estimate the elements mobility under different conditions in the environment. On the other hand, clayey sediments are an interesting object of study because of their good “accumulative properties” for trace elements. The study presented is a first attempt to apply sequential extraction procedure to differentiate the main components in clay sediments and dump materials from East Maritza Basin (EMB) by their specific suite of elements.

Material and Methods

The selection of the samples studied was based on their position and trace element content: two core samples of black clays (C-69-56 and C-3-14), two samples from internal dumps – black and gray-green clays (1998bl and 1998gr) and two samples from external dumps – mixed gray-green (SSm) and ochreous clays (G-2) of Troyanovo-2 mine (EMB). They are composed mainly of clay minerals (mixed layer illite/smectite, illite, and kaolinite group minerals), quartz, and of small quantities of gypsum, feldspar, pyrite. Organic matter is a component in black clay types only. The content of C_{org} varies from 0.39 to 2.35%.

The selective sequential extraction procedure used is based mainly on the scheme, proposed by Tessier et al. (1979) and Ure et al. (1993). It consists of the following extraction steps and operationally determined fractions: Step I. Water-soluble forms, removed by deionized water: 1 g of sample was extracted for 16 h at 25° C in 20 ml of deionized water; Step II. Exchangeable cations: the residue from step 1 was extracted for 2 h at 25° C in 10 ml of 1 M magnesium chloride solution; Step III. Carbonate fraction – acid soluble forms, associated with carbonates: the residue from step 2 was extracted for 5 h at 25° C in 20 ml of 1 M ammonium acetate adjusted to pH 5 with CH_3COOH ; Step IV. Reducible forms, associated with oxides and hydroxides of Fe, Mn and Al: the residue from step 3 was extracted for 16 h at 25° C with 40 ml of 0.1 M $NH_2OH.HCl$ at pH 2; Step V. Oxidizable forms, associated with organic matter and sulphides: the residue from step 4 was treated for 1 h at 25° C with 10 ml of 30% H_2O_2 (pH 2–3), then 1 h at 85° C and evaporated. This procedure was repeated. After cooling, the residue was extracted with 40 ml of ammonium acetate acidified with HNO_3 to pH 2; Step VI. Residual fraction – forms, associated with silicates: the residue from step 5 was digested with a mixture of HF , $HClO_4$ and HNO_3 by heating.

The extractions were conducted in a 50 ml polypropylene centrifuge tubes. The suspensions were separated by centrifuging for 20 min. at 4000 rpm and decantation of extracts, which were stored at 4° C. Between each step, the solid residue was washed with 20 ml of distilled water by shaking for 20 min. and centrifugation. The supernatant was discarded. All reagents were of chemical “pro analysi” grade from Merk and Fluka. The leachates received were analyzed by ICP-OES in Varian, Vista MPX apparatus.

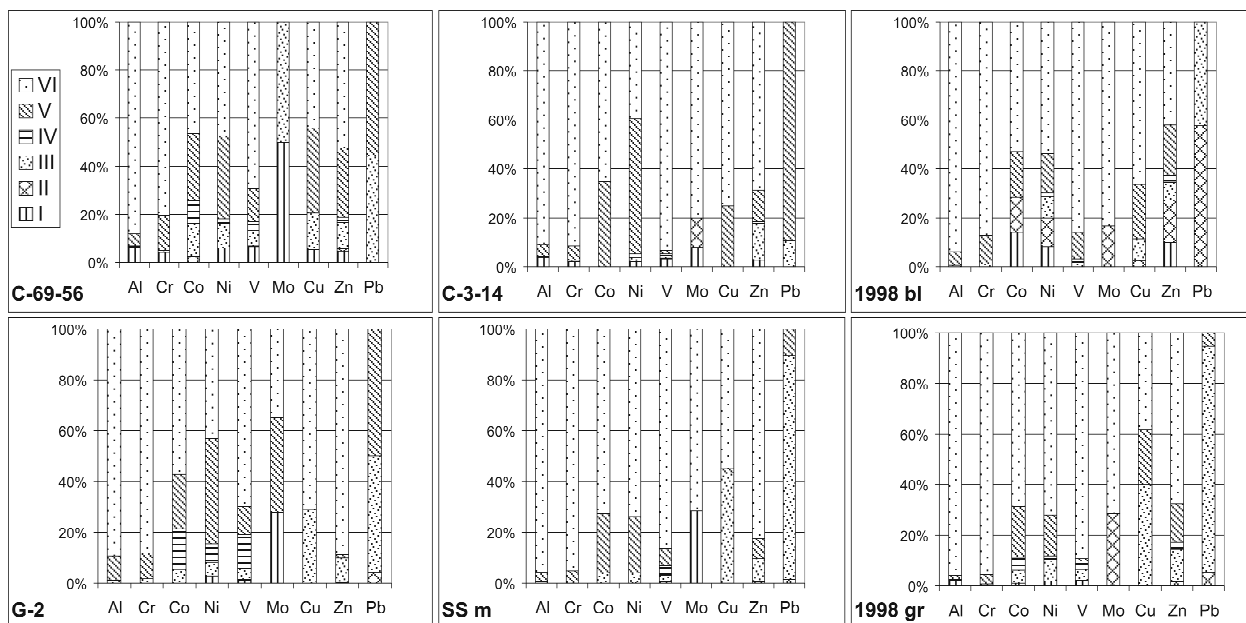


Fig. 1. Elements distribution percentages in sequentially leached fractions

Results and Discussion

The elements distribution percentages from the analyses of the sequentially leached fractions are illustrated in Figure 1. Aluminum presence and Pb absence are characteristic for all water-soluble fractions of the samples studied. Molybdenum, Co, Zn and Ni are presented individually, with high percentage in fraction I. Molybdenum reaches 50% in a water soluble form in Sm. C-69-56. Aluminum and Cr were not identified as exchangeable cations in fraction II, but Pb (>50%), Co, Zn, Mo and Ni are presented in high percentages in individual samples. "Carbonate" fraction is rich in Pb for all samples studied – from 10 to 89%, in Cu and Zn – for 5 samples, in Ni, Mo and Co – for one sample. Molybdenum was identified in one sample only (Sm. C-69-56) where it reaches 50%. As a whole fraction IV is scantily in all elements studied. The elements Cr, Co, Pb and Mo were not identified in all samples, Al presence is scantily. Vanadium, Zn and Ni are also presented in very low percentages. Individual high percentages have elements Co, V and Ni in Sm. G-2 and Co in Sm. C-69-56. The elements distribution in fraction V, connected with oxidizable forms, is very irregular. Two elements Co (20–35%) and Ni (16–42%) are abundant in all samples in the fraction. The elements Cu, Zn and Pb are also abundant, but in some of the samples. Lead reaches its maximum percentages in fraction V (90%) for Sm. C-3-14, but was not identified

in Sm. 1998bl. Molybdenum is abundant (37%) in one sample only and was not identified in the other samples. The residual fraction, associated with silicates, is the richest in all of the elements studied, except of lead – it was not identified in all samples. The percentages for most of the elements in the samples are higher than 50%, but there are some elements which do not reach 50% (Mo, Ni and Cu in two samples, and Co and Zn – in one).

The general features of the elements distribution in samples studied could be summarized as follows:

1 – most of the elements have maximum percentages in the residual, associated with silicates fraction; copper and chromium connect also with fraction V and sporadically with fraction III; vanadium and aluminum are similar in the exceptions – they have some accidental oxidizable, water-soluble and carbonate forms of presence; cobalt, zinc and nickel show irregular distribution in all fractions studied;

2 – lead shows different from the other elements behavior; it is presented mainly in carbonate and sulphide and organic matter fractions, and was not identified in water-soluble, oxidizable and silicate fractions;

3 – molybdenum is also an element with specific features; it was not identified in fraction V, and sporadically was found in fractions III and V in high percentages.

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