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Rapid method for EDXRF analysis of clayey and sandy soil[†]

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The success of quantitative full soil EDXRF analysis is strongly related to the ability establish a homogeneous and representative sample. When practicing thin-film deposition techniques the soil particle size will furthermore have an influence on the quantification capability, especially when analyzing the light elements. Finally, the deposition of material on a substrate is coupled with the sedimentation mechanism, which again is influenced by the material grain size and uniformity. In the present investigation, an effective and simple micro-milling technique for soil and sediment materials was tested. By light scattering it is demonstrated that a grain size of about 600 nm within a milling period of 15 min is obtained. The deposition of the crushed material on a polypropylene thin-film support is carried out by adding a cationic detergent, thereby obtaining a homogeneous and geometrically well defined droplet. The detergent quality and strength together with its correlation with the soil cation-exchange capacity are discussed. Clayey and sandy soil samples from different soil profiles containing a wide range of organic materials were investigated. Samples of $0.5-1$ mg cm^{-2} were analyzed by use of a monochromatic Mo Kα irradiation technique. The utility of the data fitting and quantification software X-Spec32 is discussed. A brief comment is made on the environmental aspects of soil analysis, especially in relation to metal and mineral transport and distribution through the different types of soil and soil profiles. Copyright © 2001 John Wiley & Sons, Ltd.

INTRODUCTION

In relation to environmental impact assessment and quantification of environmental pollution, the quantification of essential and/or toxicological elements in soils is an important issue. Most methods used today [e.g. atomic absorption spectrometry (AAS) and inductively coupled plasma techniques] are time consuming and often require complicated and radical chemical extraction procedures. The energy-dispersive x-ray fluorescence (EDXRF) procedure presented here represents not only an alternative to the 'classical' single-element methods but also to the related and 'competing' wavelength-dispersive XRF technique routinely applied in geochemical mapping. Both of the XRF techniques dealing with the determination of major, minor and trace elements in thick, intermediate or thin samples.[1−7]

The object of the present investigation was primarily to establish a robust, all-round full soil multi-element analytical procedure. Actually soil is characterized as the complex biogeochemical material on which plants may grow.[8] This limits not only the environment but also the physical properties of the material itself. Soil profiles deeper than

1–1.5 m are not included, and particle sizes larger than 2 mm remaining after initial disaggregation are removed.

It has further been the aim that the analytical concept should fulfil the requirement of a rapid multi-element screening procedure maintaining suitable detection limits within the full element region for correlation studies of environmental impact assessment. In addition, one should obtain a homogeneous soil sample preparation, free of textures, for the determination of a reasonably accurate and reproducible quantitative EDXRF procedure. An 'optimized' proposed compromise is presented here.

EXPERIMENTAL

Substance

From a soil analytical point of view, the principal idea has been to test a wide range of full soil textures, horizons and compositions in relation to the sample preparation and the quantitative analysis procedures. The soil textural classification shown in Fig. 1 (step 1) is according to the American (USDA) system.[8] The soil horizons (layers) are genetic designations used in the so-called ABC system especially for descriptions in the field according to FAO/Unesco guidelines. Only 'pure' horizons from an arbitrarily chosen soil are shown. In the short descriptions of the different layers, the great variability in minor elements is indicated, especially
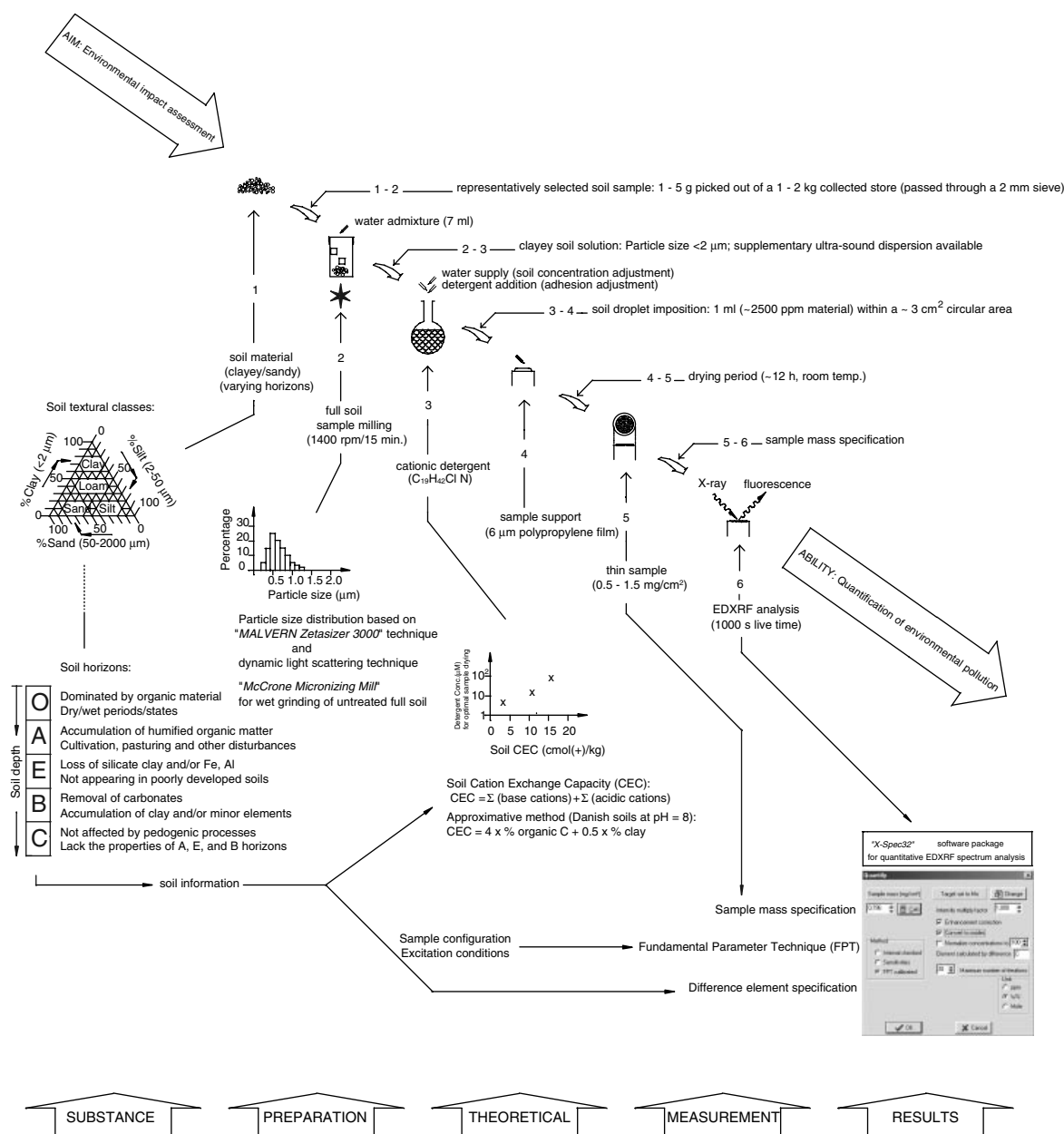
Figure 1. Flow diagram illustrating the step by step (1–6) experimental procedure.

the 'undetectable' content of carbon from (humified) organic material and carbonates important for the specification of the 'difference element' in the software quantification procedure.

Typical clayey (Farre, Denmark; 15–20% clay) and sandy (Galtlund, Denmark; 1–6% clay) soils both from strongly diverging horizons (A and B) together with Fe-enriched (A and B, Shayo, Ghana; 35–40% clay) soil types were examined.

Preparation

Typically a representatively selected soil material of 1–5 g picked out of a 1–2 kg collected store initially disaggregated and sieved to a maximum grain size of 2 mm was chosen. Subsequently the sample mixed with 7 ml of pure water was ground (Fig. 1, step 2) in a McCrone micronizing mill[9] consisting of a PVC cylindrical chamber ($d = 45$ mm, $h = 80$ mm) which accommodates 48 cylindrical corundum milling pieces ($d = 12.7$ mm, $h = 12.7$ mm). The chamber was oscillated ('shaken') at 1400 rpm for 15 min.

The particle size distribution, roughly sketched in Fig. 1 (step 2), was measured by using a Malvern Zetasizer 3000 dynamic light-scattering instrument, giving the diffusion coefficient and thereby the hydrodynamic radius of the particles (i.e. the radius of spherical particles having the same diffusion coefficient as the one measured). A supplementary and related angle dispersive light-scattering technique supported the results obtained. Grain sizes within the clay size region (<2 µm) and a medium particle diameter of about 600 nm were obtained.[10] A suitable homogeneous material was thereby obtained which further enabled the subsequent droplet sedimentation procedure to be performed.

THEORETICAL

To avoid any shrinking during the droplet drying process (steps 4 and 5, see below), a cationic detergent is added to the suspension. Based on tests with different anionic and

cationic detergents the hypothesis is that the positive end of the cationic detergent is oriented towards the negatively charged sedimentation particles, thereby directing the tail of the hydrophobic detergent towards the supporting film. This implies that the sediment will be 'glued' to the surface of the polypropylene film during the drying process.

The detergent admixture dosing seems to be sensitive to the soil type and specifically to the original texture and composition. It seems further that the soil cation-exchange capacity, CEC [CEC = Σ(base cations) + Σ(acidic cations)], is an appropriate and relevant parameter for the choice of dose. As the CEC for selected (Danish) soils at pH 8 can be approximately expressed as ($CEC_8 = 4 \times \%$ organic C + $0.5 \times \%$ clay),[11,12] it was obvious to incorporate the initial soil information about the clay and carbon content into the detergent dosing procedure (cf. step 3).

In the present investigations the cationic detergent hexadecyltrimethylammonium chloride ($C_{19}H_{42}ClN$) from Fluka was chosen. Within the concentration range 10–100 μM the contribution from chloride or trace contaminants can be neglected. The detergent is added after the milling (steps 2 and 3). Excessive shaking during the admixture should be avoided in order to prevent immobilization of the detergent in the foam. Also, cationic detergents such as $C_{19}H_{42}OHN$ and $C_{19}H_{42}BrN$ and the anionic type $C_{12}H_{25}NaO_4S$ were tested.

MEASUREMENT

By choosing the proper detergent dose, an almost perfectly homogeneous and circular-shaped thin sample layer is obtained (step 5). Based on a 1 ml droplet containing 2500 ppm (2.5 mg) of ground soil material, a specified sample area (~ 3 cm^2 ≈ 0.8 mg cm^{-2}) will be a necessary but also sufficient input parameter for the subsequent software data quantification procedure. The sample placed on a 6 μm polypropylene (Chemplex) film support in a 24 mm diameter Spectro cup is then mounted in a PC-controlled exchangeable eight-position sample holder for analysis (step 6).

The EDXRF spectrometer was thoroughly discussed elsewhere[13] and was constructed from commercially available components. A Philips compact 400 Hz x-ray generator (PW 1830/40) with a table-top 3 kW Mo anode long-fine-focus diffraction tube (PW 2275/20) is mounted on a PW 1831/00 mobile cabinet. The detector is a Kevex SuperDry 20 mm^2 Si(Li) device [FWHM (Mn Kα) = 146 eV] with a 5 μm Be window. A Kevex 4561A pulse processor is connected to a PC-based ADC and data acquisition card (Nucleus PCA3). A highly oriented pyrolytic graphite (HOPG) crystal serves as a monochromator for the incident tube radiation so that the characteristic Mo Kα line meets the Bragg requirement for $\theta = 6°$. Routinely the samples are measured at 40 kV/50 mA in 1000 s (live time).

The software package X-Spec32 is designed for full-treatment routine EDXRF analysis dealing with spectra recorded by monoenergetic excitation. In a revised version,[14] special attention was paid to the analysis of geometrically well defined thin samples having a 'dark' component of a non-detectable light element (e.g. carbon). By use of the

fundamental parameter technique (FPT) in an iterative fitting routine, full quantification including enhancement correction and oxide conversion for an *a priori* given (soil) sample density is obtained. Furthermore, an *a priori* one-element calibration allows subsequent full spectrum quantification of unknown samples within a full soil predominant element range.

RESULTS AND DISCUSSION

A wide range of full soil types, textures, horizons and compositions were examined as mentioned in the Substance section. Additionally, the agricultural soil certified reference material, NIST SRM 2709 San Joaquin Soil was included especially for testing the quantitative procedure. Selected major, minor and trace elements were additionally determined by AAS.

For all soils a 5 g/15 min milling procedure seems effective although an optimal treatment of particularly a few of the Fe-rich African soil types needed a material reduction down to 1 g owing to conglomerating effects. The detergent addition was tested through a seven-step detergent dilution series within the concentration range $1–10^3$ μM (cf. Fig. 1, step 3). Dosing outside an optimal concentration region of a decade gave rise to obviously shrinking drying sequences. Within the proposed dose range of the $C_{19}H_{42}ClN$ detergent only a few (negligible) ppm of chloride are introduced. For all the prepared soil materials a homogeneous and geometrically well defined (circular) dried sample was obtained by means of which a mass 'density' (in mg cm^{-2}) was calculated and subsequently fed into the quantitative procedure.

For the initial measurement of the SRM 2709 soil standard by use of the internal standard method (Si: 29.7%), the agreement with the reference values for the majority of the major, minor and trace elements above 10 times the minimum detection limit (MDL) was within an accuracy of 10–15% ($11 < Z < 40$; +Cs, Ba, Pb, Th). For 45 kV/50 mA (1000 s live time) MDLs ranging from 2500 ppm (Al), 1200 ppm (Si) via 70 ppm (K) and 10 ppm (V) to 1–2 ppm (Cu, Zn, ..., As, ..., Rb) were obtained. The subsequent quantification of the unknown clayey and sandy soils was based solely on the acquired information on the sample mass/area. This step was further controlled by repeated measurements on SRM 2709 thin samples (Standard error 10–15%). Supplementary AAS measurements confirmed the obtained concentrations within the major (Si), minor (Fe) and trace element (Zn) K-lines together with the heavy element (Pb) L-lines.

Perspectives

Generally the speed and reliability of this full soil analytical procedure make it suitable as a rapid screening method. Consequently the analysis of a larger number of samples may provide a better statistical foundation and thereby an improved testing of sampling procedures, soil representativity and homogeneity. The multi-element feature of the method allows for the elucidation of geochemical processes through easy and rapid analysis of co-varying element concentrations.

Regarding the environmental aspects, it might be useful in monitoring studies in which, e.g., the vertical and/or the horizontal extent of a pollution source is to be quantified. Additionally, metal mobility in soils and sediments, e.g. the detailed vertical distribution of the elements and how they are correlated among each other and with other soil variables, is to be investigated. Finally, the need for only a few milligrams of material per sample might include make it suitable for more sophisticated applications, e.g. the analysis of specific coatings and fragments from soils.

Acknowledgement

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