Physico-chemical soil analysis of Rudovci region

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Abstract. Laser diffraction and pipette methods were carried out for comparative grain-size analysis of soil samples representing a similar texture classification sampled. A detail physical-chemical analysis of soils, which involves use of XRF, XRD and SEM analysis were done. XRF and XRD analysis were done on the fractions separated by pipette method. On the obtained fraction particle size distribution and SEM analysis were done. The obtained results of these different methods are in good agreement and for detailed soil analysis comparison of both methods are recommended.

Keywords: Soil particle size distribution; Laser diffraction; Pipette methods; Microstructural analysis of soils
Introduction

Particle size distribution (PSD) is property of a soil that provides fundamental information about the size and the distribution of the soil fraction. Also it is the most often soil attribute used to characterize soil physical condition as well as determines soil mechanical, hydrological, chemical behaviours [10], soil resistance to erosion, the soil thermal conductivity [1, 2, 16, 17], soil organic matter dynamics, processes of infiltration, soil nutrient supply, seal and crust formation, among others.

Standard methods for grain-size analysis are based on sedimentation rates for the fine fractions and sieving for coarse fractions [3] the latter mainly performed with an aerometer or a pipette apparatus [12]. These methods have some disadvantages: they are time-consuming, very dependent on laboratory techniques and operator error [13], and a large amount of material is needed (at least 10 g). Such drawbacks imply that these classic techniques are not suitable for rapid, accurate analysis of a large number of samples.

Various new methods for grain-size analyses have been developed. They include electroresistance particle counting (e.g. Coulter Counter), photometrical techniques (e.g., Hydrophotometer), X-ray attenuation (Sedigraph) and laser diffractometry (LD) (e.g., Microtrac, Malvern Laser Sizer, Coulter LS). A theoretical overview of these methods that have several advantages is given in [6]. They cover a wide range of grain sizes, require only small samples, and need short analysis time. Also they may be use to analyse non-dispersed samples. The article [8] stresses the great potential of laser diffractometry in soil sciences, and it allows a detailed study of differences in aggregation that cannot be assessed by the sieve-pipette method. LD method is not a routine method and largely depends on the sample preparation and understanding of the basic physical and chemical characteristics of the sample.

When comparing pipette and laser diffraction results, one should know that the principles of measurements are different, and that both methods do not address the problem of platy particles. Advantages of the LD procedure over the pipette method include the need for only a small sample, short time of analysis, and a continuous PSD curve. Two major drawbacks of LD in relation to the pipette methods are the high cost of the instrumentation and the lack of a database that correlates LD-derived PSDs with soil properties. However, it was shown that the results of the laser diffraction method could be differed from those analyzed with the pipette method [14].

Whatever the particle-size analysis is used, the main problem is the step before the analysis i.e. pretreatment of the sample [11, 5]. Levy et al. [5] should be realized that there is no method for PSD determination of soil materials that can serve as a universal yardstick, because all available methods, whether classic (e.g., pipette) or new (e.g., LD), suffer from some inherent flaws.

The aim of this study was to compare the results concerning the determination of particle size of different fraction of soil sampled at the location of small agricultural valley Rudovci, Serbia obtained by pipette method with results obtained by laser diffraction. Also, the survey had a goal linked to the results obtained with these methods and physical and chemical characteristics of soil samples.

2 Backgrounds and Methods

2.1 Sample preparation

The area selected for the investigation was a small agricultural valley located at Rudovci tableland near Lazarevac, Serbia (44°22' N, 20°24' E). The average inclination of the slopes of the study area was 4-5° and the surface of the study area was 4 km². The samples of soil were sampled from the profile that was previously differentiated into four horizons.

The organic matter content was determined by the wet digestion method described by Mebius, 1960 [7]. Soil pH as a measure of the soil acidity was measured on a CyberScan 510 pH-meter.

The mechanical composition of samples of soil was determined by using the sedimentation method [9]. After drying, samples were sifted through 0,2 mm sif and prepared for characterization.

Microstructure and morphology of soil were recorded by X ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The crystal structure of soil before and after mechanical milling was examined by X-ray diffractometer Siemens D-500, with Cu Kα radiation. The diffracted X-rays were collected over 2θ range 20-80° using a step width of 0,02°, and measured for 1s per step.

To investigate the surface properties of the sample soil and treated one SEM analyses was carried out using JEOL JSM 6390 LV and Oxford Instrument INCA-X-sight at 25 kV.

At the mentioned location of the sampled soil mechanical fractions was done and are separated fractions of soils by pipette method. The obtained fractions were recorded with laser diffractions to verify the results of pipette method, i.e. whether the size of particles correspond to the size of particles separated by pipette method.

2.2 Pipette method

Ten grams of soil sample suspended in 1 dm³ of deionised water were passed through a set of American Society for Testing and Materials (A.S.T.M.) sieves (1000 – 32 μm). The transmitted suspension was then
poured into a 1 dm³ graduated cylinder and allowed to settle. Successive aliquots of 10 cm³ were extracted from the suspension at the time intervals calculated for a specific particle diameter (according to Stokes' law), dried and weighed. The PSD of particles <32 µm was calculated on a mass basis.

2.3 Particle size distribution by laser diffraction

Particle size distribution analysis was performed with a small-angle light scattering apparatus (Mastersizer 2000, Malvern Instruments, UK), equipped with a low-power (4mW) Helium-Neon laser with a wavelength of 633 nm as the light sources. For the particle size measurements the powder was dispersed in water, in an ultrasonic bath for 5 min. Proper selection of dispersants and the refractive index affects the measurement results. For most soil minerals a value of refractive index $n_r=1.53$ and of adsorption coefficient $n_i=0.1$ are considered suitable [4].

3 Results and discussion

3.1 Physical-chemistry and mineralogical characterization of the natural soil

The sampling sites coordinates of small agricultural valley located at Rudovci tableland near Lazarevac were determined by a Global Positioning System (Garim, GPS XL-45) (Tab. 1). Soil samples were collected from cultivated profiles which were divided on four horizons. Soil samples are labeled as $P_{1Hj}$, where $j$ denotes the in-line number of the horizons, $j = 1, 2, 3, 4$; a) $P_{1H1}$ samples from depth of 0 cm to 13 cm; b) $P_{1H2}$ samples from depth of 13 cm to 30 cm; c) $P_{1H3}$ samples from depth of 30 cm to 60 cm; d) $P_{1H4}$ samples from depth of 60 cm to 100 cm.

Table 1: Sampling spot coordinates, organic matter and pH of soil

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lat. (N)</th>
<th>Long. (E)</th>
<th>Organic matter</th>
<th>Soil (pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1H1</td>
<td>44°22'46.3</td>
<td>20°24'27.83</td>
<td>1.60%</td>
<td>5.3</td>
</tr>
<tr>
<td>P1H2</td>
<td>44°22'46.2</td>
<td>20°24'27.83</td>
<td>1.20%</td>
<td>6.1</td>
</tr>
<tr>
<td>P1H3</td>
<td>44°22'46.2</td>
<td>20°24'27.83</td>
<td>1.00%</td>
<td>6.6</td>
</tr>
<tr>
<td>P1H4</td>
<td>44°22'46.2</td>
<td>20°24'27.83</td>
<td>0.75%</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Soil pH ranged from strongly acid (4.6) to near neutral (7.6). Based on the clay content, which varied from low (55.48%) to intermediate (65.03%), the soils were characterized as light clay [15]. Tab. 2 shows contents of fraction of different horizon of cultivated soil texture includes the proportions of sand, silt and clay particle in the soil. The terms sand, silt and clay refer to different size fractions of the soil's mineral content. The sizes of clay, silt and sand are < 0.002 mm; 0.002-0.006 mm and 0.06-2 mm, respectively.

Table 2: The contents of different fraction of soil

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>Total sand (%)</th>
<th>Fine sand (%)</th>
<th>Coarse sand (%)</th>
<th>Coarse powder (%)</th>
<th>Clay powder (%)</th>
<th>Colloidal clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1H1</td>
<td>2.0-0.05</td>
<td>0.2-0.05</td>
<td>2.0-0.2</td>
<td>0.05-0.01</td>
<td>&lt; 0.01 mm</td>
<td>&lt; 0.002 mm</td>
</tr>
<tr>
<td>P1H2</td>
<td>3.2</td>
<td>2.7</td>
<td>0.6</td>
<td>41.3</td>
<td>55.48</td>
<td>19.82</td>
</tr>
<tr>
<td>P1H3</td>
<td>2.0</td>
<td>1.6</td>
<td>0.3</td>
<td>38.8</td>
<td>59.19</td>
<td>19.52</td>
</tr>
<tr>
<td>P1H4</td>
<td>2.7</td>
<td>2.2</td>
<td>0.4</td>
<td>36.2</td>
<td>61.11</td>
<td>16.55</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>2.4</td>
<td>0.7</td>
<td>31.9</td>
<td>64.95</td>
<td>14.04</td>
</tr>
</tbody>
</table>

Table 3 shows the chemical composition of four horizons of investigated soils. The data given in Table 3 shows that soil contains silica, alumina and iron in major quantities and the other elements in minor quantities.

Table 3: The chemical composition of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>ZrO₂</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1H1</td>
<td>74.93</td>
<td>4.89</td>
<td>1.72</td>
<td>3.65</td>
<td>3.27</td>
<td>0.047</td>
<td>1.22</td>
</tr>
<tr>
<td>P1H2</td>
<td>74.95</td>
<td>4.85</td>
<td>1.502</td>
<td>3.68</td>
<td>3.33</td>
<td>0.050</td>
<td>1.15</td>
</tr>
<tr>
<td>P1H3</td>
<td>68.09</td>
<td>5.402</td>
<td>1.49</td>
<td>3.74</td>
<td>4.12</td>
<td>0.038</td>
<td>1.10</td>
</tr>
<tr>
<td>P1H4</td>
<td>66.18</td>
<td>5.91</td>
<td>1.56</td>
<td>3.56</td>
<td>4.21</td>
<td>0.036</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Chemical composition of each fraction of particle is presented in Table 4. It can be seen that with decreasing of particle size amount of SiO₂ decreases and the amount of Al₂O₃ increases. Those results in different oxide ratio affect on chemical and physical properties.
Table 4: Chemical composition of soil mechanical fraction

<table>
<thead>
<tr>
<th>Particle size (mm)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-0.2</td>
<td>85.0</td>
<td>8.1</td>
<td>1.1</td>
<td>0.9</td>
<td>0.9</td>
<td>1.5</td>
<td>1.6</td>
<td>0.07</td>
</tr>
<tr>
<td>0.2-0.05</td>
<td>73.9</td>
<td>13.5</td>
<td>4.2</td>
<td>3.1</td>
<td>1.1</td>
<td>1.7</td>
<td>1.5</td>
<td>0.12</td>
</tr>
<tr>
<td>0.05-0.01</td>
<td>70.2</td>
<td>14.0</td>
<td>5.9</td>
<td>2.2</td>
<td>1.1</td>
<td>1.5</td>
<td>3.9</td>
<td>0.21</td>
</tr>
<tr>
<td>0.01-0.002</td>
<td>67.2</td>
<td>18.2</td>
<td>7.9</td>
<td>1.5</td>
<td>1.6</td>
<td>2.5</td>
<td>1.3</td>
<td>0.29</td>
</tr>
<tr>
<td>&lt;0.002</td>
<td>44.1</td>
<td>27.6</td>
<td>2.2</td>
<td>0.6</td>
<td>0.7</td>
<td>1.5</td>
<td>1.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The presence of above minerals was further tested by XRD studies. No quantitative estimation phases in these absorbents have been made but their characterization of XRD patterns indicates the presence of quartz, kaolinite and feldspar as the major phases. (Fig. 1). Clay assemblage consists of kaolinite, smectite, interstratified illite - smectite and illite. The latter contains minor titanium and some iron. Theses clays minerals represent the main components of the terrigenous detritus.

On the Fig. 2 are shown the XRD graphs of fine fractions of all four horizons and coarse fraction of sand that derived from all samples.

Comparing Fig. 2 and Fig. 1 can be concluded that the separation from deeper layers and horizons completely separate mechanical fractions from sand.
fractions (Fig. 2c and Fig. 2d). It was confirmed by qualitative mineralogical analysis of samples using XRD method. Measuring the particles size using LD method, fine fraction samples had similar values (Fig. 3). The narrow distribution implies uniform distribution as the SEM analysis confirmed (Fig. 5a, Fig. 6a, Fig. 7a and Fig. 8a).

Results of the particle size distribution, based on number, of analyzed samples of soils are presented in Tab. 5 and Fig. 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d10</td>
</tr>
<tr>
<td>Fine fraction P1H1</td>
<td>37</td>
</tr>
<tr>
<td>Fine fraction P1H2</td>
<td>35</td>
</tr>
<tr>
<td>Fine fraction P1H3</td>
<td>36</td>
</tr>
<tr>
<td>Fine fraction P1H4</td>
<td>35</td>
</tr>
<tr>
<td>Coarse fraction</td>
<td>108</td>
</tr>
</tbody>
</table>

Figure 3. Particles size distribution by LD method a) FFP1H1 (fine fraction P1H1), b) FFP1H2 (fine fraction P1H2), c) FFP1H3 (fine fraction P1H3) d) FFP1H4 (fine fraction P1H4) e) CF (coarse fraction) – sand derived from all samples

Here we emphasized that the correctness of the measurement depends on the degree of the powder dispersion. So, after 5 min of powder dispersion in water with the aid of low-intensity ultrasound, the following results were obtained: in K-type (raw sample) the particle size distribution was relatively narrow (span = 1.453) where 10 % of particles (d0.1) have diameter smaller than 108 nm, 50 % of particles (d0.5) possess diameter of 171 nm, while 90 % of particles (d0.9) are smaller than 357 nm. After 5 hours of milling, the particle size distribution become narrower (span = 1.297) and particles’ dimension where reduced, d0.1 was 34 nm, d0.5 63 nm, and d0.9 is 116 nm.

Fig. 3 presents comparative particle size distribution on four horizons of fine fractions and sand fractions. As can be seen, the particle distribution of fine fractions of all four horizons are overlapping. The particle distribution of fine fraction of the fourth horizon (FFP1H4) is practically not seen because it overlaps with the others. A narrow and uniform particles distribution of fine fractions of the fourth horizon shows that mechanical fractions are well separated by pipette method. This conclusion has been tested and proven by SEM analysis (section 3.2.).

3.2 Microstructure analysis of samples

Different sampling depths affects on the change of microstructure and morphology of the samples. The morphology of the samples is changed slightly with sampling depth because various compounds with different molecular weight participated in the pedogenesis process.

Fig. 4 show the structure of the analyzed surface soil of four horizon of the first profile in the natural state and Fig. 5, 6, 7 and 8 present samples after mechanical separation of powder fractions and Figure 9 present samples after mechanical separation of sand fractions. The surface morphology of the soil of all horizons in natural state (Figure 4) contains grains with extremely irregular shapes.

The powder makes the transition between sand and clay in size and for its other features. The powder reminiscent of flour and poorly expressed chemical resistance and when wetting indicates a low plasticity, stickiness and swelling.

Figure 4. SEM micrographs of P1H1, P1H2, P1H3 and P1H4 (horizon 1, 2, 3 and 4) samples in the natural state (magnification 400 times); a) P1H1 samples from depth of 0 cm to 13 cm; b) P1H2 samples from depth of 13 cm
to 30 cm; c) P1H3 samples from depth of 30 cm to 60 cm; d) P1H4 samples from depth of 60 cm to 100 cm

Unlike sand it's in the dry state has a hard consistency. Due to expressed capillarity, a powder fraction has sustainability of water, good to medium permeability and high ability for increasing water by capillary effects, where the capillary rise much slower than in sands.

![Image](image1)

As seen on Fig. 5 powder particles are in the range from 55.73 µm up to 124.23 µm, while agglomerates of sand are in the range from 152.49 µm up to 282.44 µm (Fig. 9). Micrographs at magnifications of 2500 times show a clear distinction on the basis of pore patterns. In samples of sand observed agglomerates are pronounced macro-porosity. With soil depth, micro-capillary pores increase and this is the reason why the powder particles show in some degree physical and chemical properties of clay.

![Image](image2)

SEM images of powder samples after the pipette method done by mechanical separation of particles with a depth from 13 cm up to 30 cm were shown on the Fig. 6. According to Fig 6 and comparing arrangement of particles presented on these figures (Fig. 6 and Fig. 4a), one can notice uniform distribution of particles.

![Image](image3)

SEM images of powder samples after the pipette method mechanical separation of particles with a depth from 30 cm up to 60 cm were shown on the Fig. 7. Figure 7a shows a uniform arrangement of particles. Particles size are in range of 61.80 µm to 148.20 µm (Figure 7 b).

![Image](image4)

Figure 7. SEM images of powder samples after the pipette method mechanical separation of the first profile with a depth from 30 cm up to 60 cm (a -90 times magnification, b -90 times magnification (size of crystallites are labelled), c - 400 times magnification and d -2500 times magnification)

On the Fig. 7c (magnification - 400 times) the kaolinite and quartz particles are detected. On the Fig. 7d (magnification - 2500 times) kaolinite particles are also detected with capillaries and cracks that are responsible for the migration of polluting substances through the soil (depth - 30 cm up to 60 cm).
Figure 8. SEM images of powder samples after the pipette method mechanical separation of the first profile with a depth from 60 cm up to 100 cm (a -90 times magnification, b- 90 times magnification (size of crystallites are labelled), c -400 times magnification and d -2500 times magnification)

SEM images of powder samples after the pipette method mechanical separation of the first profile with a depth from 60 cm up to 100 cm are presented on the Figure 8. The uniform distribution of particles after mechanical separation of soils is confirmed once again (Fig. 8a). Particles sizes in the horizon with a depth from 60 cm up to 100 cm are in the range from 63.98 µm to 129.20 µm (Fig. 8b).

SEM micrographs of sand samples after the pipette method mechanical separation are shown on the Fig. 9. Figure 9. SEM images of samples of sand after pipette method mechanical separation a -90 times magnification, b-90 times magnification (size of crystallites are labelled), c-400 times magnification and d-2500 times magnification)

The uniform arrangement of particles is observed (Fig. 9a) and particles of sand are larger than powder particles that might be expected (Fig. 9b). The size of agglomerate ranged from 162.49 µm up to 347.07 µm. At magnifications of 400 times were recorded on kaolinite particles, which are still recorded at magnifications of 2500 times.

Based on these results, one can conclude that the separation of soils using the pipette method gives uniform samples. A comparison with natural samples of soil horizons at the same profile can be seen that after the separation of soils using the pipette methods agglomerates are composed of identical fractions. The results of SEM analysis confirmed the results of pipette method, i.e. properly separation of fractions of soil and confirmed that the results of mechanical composition of soil were obtained by using of good method.

4 Conclusion

Particle sizes were determined in the profile where the mineralogical content was constant. Based on the results, one can conclude that the fine fraction separate is uniform as confirmed by the PSD method and by SEM analysis. Reduced presence of quartz in the fine fractions in deeper horizons was detected using XRD analysis. Finding the appropriate reference values directly from the soil samples, can be used for particle size distribution analysis.

Particle size of feldspars which is determined by XRD analysis, matches with PSD analysis. Using laser diffraction instead of pipette method simplifies determination of soil texture and accelerates the time of analysis. Obtained results of both methods are in good agreement and in the future pipette method can be completely replaced with laser diffraction method.

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References


