

## FTIR photoacoustic spectroscopy of soils: comparison of FTIR modalities for soil fractions of various agrogenesis

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Granulometric fractionation as a source of additional information on organic-matter and inorganic matrix components of soils using FTIR photoacoustic spectroscopy (FTIR PAS) supported by attenuated-total reflection FTIR spectroscopy (ATR–FTIR) and diffuse reflectance FTIR (DRIFT) for a wide range of aggregate fractions (10–5000  $\mu$ m) was used to compare the sensitivity, reproducibility, information contents, and representativity of fractionated samples. FTIR PAS modality shows a much higher sensitivity in the middle-wave range (SiO<sub>2</sub> overtone range) of the mid-IR range than attenuated total reflection modalities and excels diffuse-reflectance modality as it does not require sample dilution. In addition, FTIR PAS measurements are possible for soil aggregates up to 5 mm without sample decomposition or milling

The studies of the influence of agrogenesis and anthropogenesis on the physical and physicochemical properties of soils experience a notable shift. Apart from traditional approaches to assessing bulk soil properties, the new information level requires determining soil fractions and aggregate structures, including the changes at meso- and microaggregate levels.

FTIR Photoacoustic spectroscopy is a sensitive modality of absorption spectroscopy. It is based on the measurements of the heat caused by the absorption of radiation by the sample. The pressure waves resulting from heating the sample by IR or visible light are detected by a microphone or a piezo-transducer, providing high sensitivity of light-absorption measurements. FTIR PAS features depth profiling, simple and almost non-destructive sample preparation, and small amounts of the test sample.

This study aims to work out the approaches for the identification and assessment of inorganic and organic-matter components of bulk samples and size fractions (by dry sieving) of chernozems and sod-podzolic soils as SiO<sub>2</sub>-based soils with a different type of land use by FTIR PAS. Mid-IR PA spectra of size fractions 1–5000 mm were studied. The conditions of FTIR PAS measurements were compared with attenuated-total-reflection (ATR) and diffuse-reflection (DRIFT) measurements. Apart from depth analysis, FTIR-PAS provides relatively reproducible conditions for various size fractions, and these fractions hold more differences than entire soils.

FTIR PAS modality shows a much higher sensitivity in the middle-wave range (SiO<sub>2</sub> overtone range) of the mid-IR range than attenuated total reflection modalities and excels diffuse-reflectance modality as it does not require sample dilution. In addition, FTIR PAS measurements are possible for soil aggregates up to 5 mm without sample decomposition or milling, which is a unique property of this modality [1].



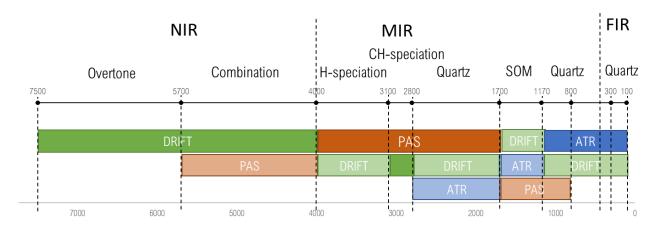


Fig. 1. Applicability of DRIFT, ATR–FTIR, and FTIR–PAS for qualitative analysis for silicate soils. Applicable techniques are shown in full colors, ambiguous, in watercolors, the most informative technique in each subrange is shown at a higher position [2].

For studied silicate-based soils, matrix minerals are dominant in the whole spectrum despite a high concentration of soil organic matter. Therefore, the organic-matter analysis is impossible without destructive sample preparation, organic-matter extraction, or some not-so-obvious assumptions. On the contrary, the inorganic-component analysis appears to be more promising for non-destructive FTIR PAS as it can be based on large mineral databases and approaches to quantitative assessment based on mineral bands of different origins. An essential feature of FTIR PAS of studied soils is that quartz overtone peaks at 2000–1700 cm<sup>-1</sup> can be used as internal standards of soil samples of the same type for more balanced spectra comparison.

A drawback of FTIR PAS is rather sophisticated data processing, which is a considerable asset in basic research of soils but is rather inappropriate for serial or rapid analysis of multiple samples in large-scale experiments. Therefore, some strict but simple data handling algorithms are required for more reliable and reproducible data in FTIR PAS. Still, the developed methodological approaches and previous findings seem reliable enough for use in soil analysis, including meso- and microaggregate levels.

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## References

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