Photoacoustic and photothermal methods in spectroscopy and characterization of soils and soil organic matter

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A R T I C L E   I N F O

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A B S T R A C T

Review sums up the application of photoacoustic and photothermal spectroscopies for the analysis and characterization of soils and soil organic matter and discusses the outlooks in this area.

1. Introduction

Soil is a fundamental natural resource and it provides most of the geophysical and biochemical interactions of the Earth surface with the atmosphere and groundwater. According to state-of-the-art concepts, soil is a continuous multicomponent organomineral system of high complexity, of several dozen thousands of substances [1–3]. Soil organic matter (SOM; sometimes, soil organic carbon [SOC]) is an ensemble of high- and low-molecular organic and inorganic substances that form a single organomineral entity in a finely dispersed state. SOM is a part of the pool of non-living natural organic matter. The latter is historically split into two parts: soluble and dispersed organic matter (DOM; insoluble organic matter [IOM]; or kerogen) [4–6]. This classification appeared as the easiest way to study organic compounds in rocks by their extraction with widespread organic solvents (alcohols, benzene, chloroform, carbon disulfide, etc.) or their mixtures. Thus, DOM is usually defined as all the insoluble dispersed sedimentary organic matter, including not only dispersed in sedimentary rocks, but also “purely” organic deposits such as humic and algal coals, humin in soils, and various asphaltic substances [7]. SOM comprises the majority of the non-living natural organic matter; it can reach up to 99 %, while only a small part (1 %) of organic matter is soluble in organic solvents [6,8]. SOM shares the origins and complexity of DOM and all above-discussed is true for soils and its organic matter [1–3].

The problem of studying DOM and SOM has been and remains quite relevant, as it is the main part of all organic matter and a major organic sink in the global carbon cycle on Earth [9]. The first studies of DOM were made in the 19th century [10,11], although active systematic research has started in 1960s, mainly in geochemistry, with a wide range of instrumental methods [10–14]. Still, DOM is known much less compared to soil mineral components due and many informative methods for the latter: X-ray, optical atomic, electron microscopy, etc., and its relative simplicity. From 2000–2019, more than 4800 studies (according to Web of Science®) have been published titling ‘soil organic matter’ with the exponentially growing number, more than 40 % (about 2000) published over the past five years. Advancing the principles for investigation and characterization of DOM, its structure and transformation is quite topical.

The challenge of this problem lies with the concept of DOM (and SOM) itself, which is based on properties—soluble or insoluble—rather than on chemical structures explicitly. Indeed, extraction is quite practical providing chemical fractionation and separation as well as simplifying complex DOM mixtures prior chromatographic or spectrochemical studies. But in the same time, such an indirect classification results in the information only on some part of DOM from each method, hardly giving the whole picture. Pyrolysis and thermogravimetry in combination with chromatography and mass-spectrometry [15]—as based on a somewhat directed or controllable decomposition of the starting material—implicitly show the structure of intact DOM. NMR and chromatography provide the information about specific parts of molecules, moieties, or structural fragments rather than the whole ensembles. Methods of solid-state chemical analysis (fluorescence...
spectrometry, X-ray absorption near-edge spectroscopy (XANES), solid-state $^1$H and $^{13}$C NMR [16–18], and CHONS-analysis) also hardly present individual molecular structures of the sample as well. Only the combination of these methods allowed proving the existence of many polycyclic aromatic moieties in DOM [19–21]. Nowadays, the most complete description of DOM is achieved by pyrolysis GC × GC-TOF MS [20]. On the basis of combination of methods giving different information levels (solid-state NMR, electron paramagnetic resonance, XANES, and high-resolution electron microscopy combined with thermal and chemical decomposition), a structural model of DOM was proposed [22]. The state of the art is that DOM is composed primarily of highly substituted single-ring aromatics and furan/pyrrol moieties, highly branched oxygenated aliphatic substances, and carbonyl groups [17,23]. Still, complex macromolecular structures of DOM require more detailed studies from the viewpoint of structural-group composition [24,25]. The latter is crucial for a qualitatively new, non-empirical concept of DOM—based on chemical structures and the data of state-of-the-art methods of analysis—ultimately to classify DOM as its own class of compounds. This is one of the main challenges of chemistry.

Thus, the methods for direct characterization of individual molecular structures in DOM or its whole ensemble are crucial [26]. The significant progress in the last two decades both in the instrumentation and methodology led to revolutionary inventions [27–31]. The development of such highly informative methods as Fourier-transform ion-cyclotron-resonance and Orbitrap mass spectrometries led to the concept of non-target analysis of DOM [18]. This brand-new strategy looks at DOM from a molecular point of view and monitors the dynamics of its entire changes. This unraveled the existence of many tens of thousands of compounds [18,32,33]. However, these methods still require sample preparation (extraction and/or chemical fractionation). In the context of SOM, researchers actively work also at the physical (granulometric and densimetric) fractions of soil, including soil colloids and aggregates [24–42], which gives yet another level of detail, but it does not directly provide chemical information as well.

Molecular spectroscopy (primarily, fluorescence and vibrational spectroscopies) holds a rather obvious but unique position in the context of studying the molecular composition of soils, especially the structural-group composition of SOM [43–45]. On the one hand, it does not require the dissolution of samples and their modification to obtain structural-group information about the entire soil composition including SOM. On the other hand, these methods work in solutions obtained after extraction, which makes it possible to compare these data with NMR, mass-spectrometry, or other methods. Still, fluorescence and transmission/reflection spectroscopies have some disadvantages. The former is usable for a limited number of fluorescent substances only and is prone to many interfering factors. For such complex mixtures as DOM or SOM, wide bands of optical absorption and fluorescence spectroscopies are quite difficult, if almost impossible, to interpret due to the overlapped bands, and not all the techniques work with powdered samples.

IR spectroscopy has been used in studies of soils and SOM for a long time, but over the past two decades its role has increased dramatically due to a new technological level achieved [46–50]. Novel broadband detectors and beam splitters have appeared, and the detection sensitivity has increased significantly. To date, characteristic limits of detection are 0.01 %–10 % w/w with a relative standard deviation of 0.05–0.20 [%1,52]. Many techniques were implemented: diffuse and specular reflectance modalities for a wide range of temperatures and pressures, attenuated total-reflection (ATR) modality with a variety of crystals and beam-incidence angles, FTIR microscopy, etc. This made it possible to assess both organic and inorganic substances simultaneously and obtain the information from depths from tens of nanometers to tens of micrometers. IR spectroscopy has advantages over optical spectroscopy, mostly due to a combination of advanced techniques, sample preparation, and data-processing algorithms [46–50]. E.g., diffuse-reflection IR spectroscopy is widely used in quantitative soil analysis already [49,53–55]. However, the size distribution of soil particles seriously affects the diffuse-reflection IR spectra and leads to high measurement errors even for the same sample. Another widely used variant is ATR FTIR spectroscopy. However, dry samples of soils do not provide good contact with the ATR crystal, which degrades the sensitivity and precision of measurements, while adding wetting agents seriously distorts the results, which significantly narrows the applicability of this method [56].

Photoacoustic and photothermal spectroscopies (PAS and PTS, respectively) complement transmission/reflection methods like spectrofluorimetry, spectrofluorimetry, and conventional absorption IR spectroscopy. In transmission/reflection methods, the transmitted or reflected (i.e. non-absorbed) part of the electromagnetic radiation is measured, whereas photothermal and photoacoustic methods are based upon non-radiative transitions of excited molecules caused by the absorbed part of the radiation passed into the sample. PAS and PTS are among the most sensitive methods of molecular-absorption spectroscopy and can be used for the whole range of molecular structures contrary to fluorophore-specific fluorimetric methods [57,58]. Also, as PAS and PTS are based on thermal-relaxation processes, they are suitable for the characterization of thermal properties of materials.

This provides a rather unique place of PAS and PTS within the realm of molecular spectroscopy. The number of applications in various areas of these methods grows exponentially, and relatively recently, they have appeared in Earth sciences [59–71]. Still, in our opinion, summing up their possibilities in solving the problems of DOM and SOM discussed above is lacking. Thus, the aim of this review is to summarize the use of methods of photoacoustic and photothermal spectroscopies for the analysis and characterization of SOM and soils and to discuss the main applications and outlooks of these techniques.

2. Methods of photoacoustic and photothermal spectroscopies

Photoacoustic and photothermal spectroscopies comprise calorimetric spectroscopy, which is defined as the methods for measurement of thermally relaxed radiation absorbed by matter [57,58,72,73]. They are based on the absorption of the electromagnetic radiation by sample components and thermal relaxation of the absorbed energy by the whole sample through heat transfer and secondary emission. As thermal relaxation leads to heating the sample, these methods acquire the information carried by the optical (photothermal or thermooptical spectroscopy, PTS) and/or acoustic (photoacoustic or optoacoustic spectroscopy, PAS) responses of the sample. In all photothermal and photoacoustic methods, the signal is directly proportional to the power (radiance) of the radiation that excites (induces) photothermal effects. In this sense, PTS and PAS have the same feature as fluorescence spectroscopy: by increasing the excitation power, it is possible to increase the sensitivity, but for non-fluorescing molecules, moieties, or particles.

2.1. Photoacoustic (optoacoustic) spectroscopy

The photoacoustic (or optoacoustic) effect consists in a change in the pressure (acoustic pulse, PAS signal) caused by thermal expansion of the sample upon the absorption of electromagnetic radiation by its molecular structures leading to local heating of the sample and subsequent nonradiative relaxation [74,75]. This change in pressure is detected with a microphone or piezo transducer [70,76]. Introduced by J. Bell over 100 years ago for gases, the state-of-the-art PAS has started with the appearance of laser excitation sources. From 1980s, PAS is being successfully applied also for condensed systems as the basis of the physics underlying the photoacoustic effect has been developed [77]. Currently, PAS experiences the great boost of studies for biomedical microscopy, imaging, and tomography in vivo [78–91], which are out of the scope of this review.

Most PAS techniques are relatively simple and characterized by a
wide linear signal range, good rapidity, small volumes of test samples, and the ability to automate measurements [58]. From the practical implementation, there are two varieties of PAS, like in transmission spectroscopy. The first one is single-wave or scanning spectrometry based on lasers or NUV/vis/NIR lamps. The second variant is the application of simultaneous PAS modalities, usually as parts of FTIR interferometers.

Single-wave PAS is widespread in biomedical microscopic imaging as well as in the assessment of material properties. Single-wave measurements provide a high speed of measurements and are used when the major chromophore is known (e.g. haemoglobin or a tag in biomedical imaging) [82,83,88,90]. The research with single-wave PAS is also associated with thermal parameters of homogeneous solid materials or processes in solutions, when a reliable and powerful but not tunable excitation by a laser is required, but this results in a lack of spectral information. Currently, the number of wavelengths in these modalities increases, which resulted in the implementation of multispectral PAS, especially multispectral PAS microspectroscopy or tomography [81,86,92]; and this trend is similar to fluorescence and Raman microspectroscopies eventually shifting to hyperspectral imaging [93–95].

In the case of interferometric PAS techniques, the measurement is based on single-dimensional heat transfer models in solids and gas-phase detection [58,96,97]. The IR beam from the interferometer is directed to the PAS unit and focused on a test sample in a closed compartment filled with a working gas with a limited and known volume. Interferometer-modulated IR radiation is absorbed by the test sample and converted into heat. These periodical temperature changes in the sample (thermal waves) depend on the interferometer modulation frequency, absorption coefficients of sample constituents, and thermophysical parameters of the sample. Thermal waves generated from the sample, from the depth limited by the thermal-diffusion length (thermal-wave decay length) move into the working gas [58,96,97]. As a result, thermal waves generate pressure (acoustic) waves in the working gas that are detected with an acoustic detector located near the main axis of the PAS unit.

In interferometric PAS techniques, the spectral information is crucial and almost always is the major aim of measurements [58]. Due to the most information on molecular structures and moieties is believed to be held in the mid-IR region, most studies are made in this spectral range and from this point on, we will use the abbreviation FTIR-PAS for this modality. In FTIR-PAS, two working modes of the interferometer are used: the conventional, normal (continuous) scan of most commercially available FTIR instruments (rapid or slow-scan modes, as rather low frequencies of the interferometer are usually needed for thin layers) or the step-scan mode. In normal-scan operation involving mirror translation, the mirror velocity is calibrated using a single wavelength and held constant upon data acquisition, whereas in a step-scan operation it is the spacing of the moving mirror that is held constant (with a precision of a few nanometers) during data acquisition. Normal-scan operation is convenient, but due to the different frequencies corresponding to the different wavelengths, it produced different signal-generating depths in the final spectrum, especially in the IR range. To the contrary, a step-scan mode controls the velocity of the moving mirror of the interferometer; in all the serially produced interferometers, this involves the use of a parallel or collinear laser interferometer for accurate data spacing [98]. Thus, step-scan operation of interferometric PAS (referred to as photocoustic step-scan FTIR) provides a constant modulation frequency of measurements, and thus, the constant signal-generating depth over the entire spectral range. This modality usually involves a lock-in amplifier or digital signal processing methods to detect and amplify the photocoustic signal [99].

For solid samples, a key advantage of all the modalities of PAS is the possibility of obtaining spectra without sample preparation and dilution [100]. Another important advantage is the possibility of depth-profiling solid samples within a few hundred micrometers by varying the frequency/velocity of the radiation source [101–103]. Compared to diffuse-reflection spectroscopy, PAS is less affected by the sample particle size [104]. Compared to ATR techniques, PAS shows higher sensitivity, while the signal is much less affected by radiation scattering [105].

From the practical point of view, PAS is used to directly determine absorption coefficients of materials and their constituents up to 1000 cm⁻¹. Due to linear dependence of the photoacoustic response on the light-absorption coefficient, PAS is used in the assessment of analyte concentrations in gaseous, liquid, and solid media in a wide dynamic range (10⁻⁴–10⁻¹ absorbance units) and with a high precision (up to 0.1 %) [74,106]. Thus, PAS provides a wider range than common transmission absorption measurements (spectrophotometry) and higher sensitivity. The detection of main gases and trace levels of pollutants in the gas phase is one of application of PAS. Detection limits in PAS in solutions are 0.1–1 ng mL⁻¹ in the visible region and up to 0.1–1 µg g⁻¹ in the IR region, which is used for objects of different nature [107]. In complex samples, apart from biomedical applications, most widespread PAS application is characterization of nanoparticles and nanomaterials [108–118]. In the case of solid samples, various modalities of PAS are used for polymeric materials [119], minerals, and soils that are discussed further on.

2.2. Photothermal spectroscopy

PTS is closely related to PAS and is based on other subsequences of thermal relaxation of the absorbed energy. Namely, it is the formation of a nonuniform spatial profile of the refractive index of the sample (thermooptical effects, and thermooptical methods of PTS) and secondary thermal emission of the sample (photothermal radiometry methods). Photothermal spectroscopy is an umbrella term for the whole variety of these methods. Thermooptical methods of PTS usually rely upon a form of the spatial profile resembling a specific optical element (lens, mirror, diffraction grating, etc.) [57]. The application of thermooptical methods is based on the fact that the characteristic parameter of the thermooptical element (like the focal strength of a thermal lens in thermal-lens spectrometry) is directly proportional to the light-absorption parameters of the sample and, hence, to the concentration and absorption coefficient of the test compound. As in the case of PAS, though to lower extent, the thermooptical signal is less affected by light scattering compared to conventional absorption spectroscopy.

Thermal-lens spectrometry is a most widespread photothermal method in solutions and is used in applied chemistry. Thermal relaxation in a sample results in a nonuniform refractive-index spatial profile acting like a lens (a thermal lens effect). Its optical strength is proportional to the sample absorbance and, thus, to the absorber concentrations and absorptivities. Thermal-lens spectrometry provides the detection of absorbances at the level of 10⁻⁹–10⁻⁶ absorbance units (corresponds to concentrations of test substances in solution down to 10⁻¹¹ mol dm⁻³) in volumes of 10⁻¹² L [57,120]. These values are at least two times lower than conventional transmission measurements, and photothermal methods are considered more sensitive than most modalities of photoacoustic spectroscopy; however, the linearity of photothermal modalities (usually, ca. 3 orders of magnitude) is somewhat comparable to conventional transmission measurements and narrower than photoacoustic measurements due to a nonlinear character of the parameters of optical elements used as approximations of models for concentration-dependent linear signals (model limitations) [57].

Among thermooptical methods for solid samples, photothermal beam-deflection spectroscopy (PBDS or photothermal deflection spectroscopy, PDS) is one of the most widespread methods both in the optical and IR ranges [57,121–124]. A modulated (NUV/vis/NIR) beam is focused onto a flat-surface sample, and the excitation radiation absorbed by the specimen results in thermal waves and a temperature field in both the sample and contact medium (air, purge gas, or a contact...
liquid) over it. Thermal relaxation brings about a refractive index gradient in this medium. This leads to the deflection of a probe beam that propagates parallel to the sample surface in the contact medium (mirage effect) or hitting the sample at a certain angle (photothermal mirror). Apart from high sensitivity and dependence on the thermal diffusivity of the sample, the advantage of PBDS is that sample preparation can mostly be avoided for complex samples. Thus, the surface of a specimen can be examined directly, provided that the probe beam passes over the sample area. A minimal sample preparation, consisting of slightly grinding the sample, increases the sensitivity and avoids spectral reflection effects.

Photothermal radiometry is used for surface and layer absorption and is a heat-wave technique [57,63,125–127]. The partial absorption of modulated/pulsed laser radiation and the release of heat result in thermal waves. Unlike in PAS and PBDS, the thermal diffusion length of the material characterizes the thermal-wave penetration depth to which photothermal radiometry is effective. The excited sample emits secondary IR radiation due to thermal relaxation, which is detected by an IR detector. The amount of radiated energy is proportional to the absorption coefficient of the specimen. In photothermal radiometry, the signal development rate is significantly higher relative to other photothermal methods. It is accounted for the fact that the development of surface deformation and the temperature gradient in the environment requires a considerable time in comparison with the thermal relaxation time. The advantages of photothermal radiometry are the features of remote sensing, the simplicity of the experimental setup, and high spatial and time resolutions ($10^{-6}$–$10^{-5}$ s, down to $10^{-6}$–$10^{-5}$ s for pulsed radiometric techniques). The spatial resolution is determined by the focussing of the excitation radiation and is the same as for other photoacoustic and photothermal techniques. Time resolution of photothermal radiometry is determined by the response of the secondary radiation detected by thermal or IR detector modalities and is limited by their response time [126,129]. All this makes it possible to measure the spectra of intermediate products and to investigate rapidly occurring processes, including depth-resolved studies [129–132]. A photothermal-radiometry technique called opto-thermal transient emission radiometry (OTTER) provides noninvasive and noncontact recording of absorption spectra of any surfaces including human skin and complex technological samples [133,134].

### 2.3. Thermal mapping and characterization

PAS and PTS provide the information about the material parameters associated with the heat distribution (thermal diffusivity, thermal conductivity, heat capacity, refractive index, density, viscosity, etc.) directly from the obtained signal. Moreover, in addition to stationary signals corresponding to the attainment of thermal equilibrium for photothermal phenomena, which are mainly used in the measurements of light-absorption parameters, transient parameters of the formation and dissipation of photoacoustic and photothermal effects (time-resolved signals) significantly depend on the thermophysical parameters of the medium and on possible ways of absorbed energy conversion rather than the light absorption (unlike stationary signals), first of all, on thermal diffusivity. Thus, it is possible to calculate the heat capacity and thermal conductivity of the sample from these data [135–139].

As PAS and PTS usually have a micrometer- or nanometer-scale spatial resolution, they provide thermal mapping or imaging of complex specimens with high reproducibility and resolution. As a widespread application, they are used for micro/nanoscale defects in various materials including optical coatings [140–142] or in the depth of heterogeneous materials [143]. It is shown that the amount of particles and their size make a critical effect on the formation of the thermo-optical response of solid nanocomposite polymer materials and on the development of a thermal profile [144,145].

### 3. Photoacoustic and photothermal assessment of minerals

Photoacoustics of solely mineral samples (also rocks or artificial mineral-like materials) is a separate and rather developed branch of photothermal and photoacoustic measurements and is generally out of scope of this review. The basic principles of PAS of minerals are formulated in early 1980s [62] and the most characteristic examples are summed up in the rather recent book by Michaelian [58]. Recent developments in this area are also connected with thermal parameters of minerals or the application of single-wave PAS to the characterization of complex organomineral specimens, e.g. artificially changed minerals like geopolymers or protection films on stone surfaces [59,146,147]. Also recently, photoacoustic modalities for mineral and mineral nanoparticles like magnetite or vaterite have started to appear in photoacoustic biomedical imaging as such nanoparticles are on demand as multimodal contrast agents, drug delivery systems, or optical sensing materials [119,148].

PTS is less widespread in studies of minerals compared to PAS, the studies are also connected with the characterization of rocks suitable for building industries, and the main area is thermal rather than spectral characterization, which is discussed below (see Section 7 below). Photothermal IR spectra of minerals are recorded by PBDS with minimal sample preparation and even with no sample preparation at all [64]. Measurement of the beam deflection results in the IR photothermal absorption spectrum, examples of application of the technique to carbonate and lead minerals are shown [64]. In PTS, the studies of minerals also shift to microscopometry and complex studies of organomineral complexes.

### 4. Photoacoustic spectroscopy of soils

The difference between soils and minerals is a developed surface, a natural extremely high heterogeneity, granularity, and a combination of organic and mineral parts, both of which are important for the interpretation of spectra and related conclusions. In addition, soil particles have a complex structure and are mineral cores of different sizes (commonly represented by layered silicate-clay minerals), coated and/or bonded with amorphous organic or organomineral films of various composition [149–153]. Thus, both the structure and composition of soil samples are very variable. This seriously distinguishes the soil from other organic samples, including polymeric, organo-metal, or technological samples, whose structure and composition are rather well known, as well as from most biological macromolecules with a known structure. All this requires the development of specific approaches for all the methods of molecular spectroscopy of soils.

In the case of PAS of soils, historically first were measurements of soil using optical-range excitation sources. But as it required rather sophisticated data processing and much more information can be obtained from the more informative mid-IR range, PAS soil studies in the last decade shifted to FTIR-PAS [65–70,76,154–160]. The studies with the optical excitation shifted to thermal measurements like in the case of minerals. Thus, in the following subsections, optical and IR PAS modalities are considered separately.

#### 4.1. Optical photoacoustic spectroscopy of soils

The theory of application of optical PAS for soils as well as clay minerals was evolved in 1980 [62]. It was shown that PAS provides absorption spectra of soil and clay minerals throughout the NUV, visible, and NIR ranges, which are difficult to study by transmission or reflectance spectroscopies due to sample heterogeneity and light-scattering artifacts. This paper [62] was first that showed the possibilities of difference techniques of PAS in assessing low amounts of chromophores in soil-type samples and seeing the interactions of mineral components and SOM.

The practical application of optical PAS is the assessment of
indicating the positions of absorption bands associated with the electronic transitions of the Fe(III) in octahedral sites of kaolinite structures. Photoacoustic and characteristic thermal diffusivities and supported with theoretical calculations and radiometry. Solar energy absorption was modeled as related to surface temperatures of several types of soils were measured by PAS and the solar energy for the correspondent wavelength intervals along with mineralogical composition of soil samples from combined used of PAS and X-ray diffraction [161,162]. Photoacoustic spectra showed transition bands associated with ionic Fe(III) species with octahedral or tetrahedral symmetries and supported with theoretical calculations (Fig. 1). From the phase behavior, both the nonradiative relaxation time and characteristic thermal diffusion time can be determined. Rietveld refinement of X-ray data showed that Fe(III) partially substitutes for Al (III) in octahedral sites of kaolinite structures. Photoacoustic and conventional absorption spectra in 200–2000 nm by the ground surface of the solar energy for the correspondent wavelength intervals along with surface temperatures of several types of soils were measured by PAS and radiometry. Solar energy absorption was modeled as related to SOM and Fe₂O₃ content [71].

Another problem solved by optical PAS in soil analysis is in situ rapid assessment of heavy-metal pollution as this strongly impacts the human-health issues and environment. Rather recently, a cost-effective broadband NIR PAS system (Fig. 2) without the involvement of complicated sample pretreatment has been proposed for the assessment of Pb contamination in soil [163]. NIR PAS absorption spectra of model samples of soils contaminated with Pb show a decrease in O–H overtone bands at 1400 and 1900 nm with an increase in Pb concentration, although with the expected low sensitivity still.

The most recent study shows a full-fledged NIR-PAS (800–2400 nm) soil analysis concept [157]. An experimental setup consists of a photoacoustic accessory, tungsten-bromine lamp, monochromator, chopper, and lock-in-amplifier [157]. Partial least-squares regression (PLSR) model and cross-validation were used to predict SOM, clay, carbonate, and available phosphorus content from PAS data. It was found that SOM significantly affected the spectra, and the intensities and positions of 1st to 3rd overtone and combination absorption bands in the range of 880–2200 nm (O–H, N–H, and C–H) significantly shifted owing to the variances in the content and structure of SOM (Fig. 3). The PLSR model is claimed to be successful in SOM prediction of with a root mean square error of 2.5 g kg⁻¹ and a ratio of standard deviation to prediction error of over 2 [157].

4.2. IR photoacoustic spectroscopy of soils

Photoacoustic spectroscopy can be used to determine the chemical properties of main components of soils. The bands corresponding to the fundamental vibrations of organic soil components are in the mid-IR range as well as fundamental vibrations and overtone and combination bands of inorganic constituents [164,165]. The NIR range contains overtones and combination bands of organic matter and low-molecular compounds of soil. Soil minerals, such as different types of clays, have distinct absorption bands due to strong absorption caused by overtones of SO₂²⁻, CO₂²⁻, OH⁻ and combinations of fundamental vibrations of H₂O and CO₂ [166,167], which made it possible to identify some soil samples by their IR spectra [168]. IR PAS has a number of advantages over other methods of IR spectroscopy for soils: IR PAS spectra show more well-defined bands in comparison with ATR spectra, and also the range in which the informational spectrum is recorded is wider (owing to the fact that the 4000–1600 cm⁻¹ region in the ATR spectra is occupied by strong absorption bands of liquid water) [168,169]. For carbonate-based soils, ATR spectra contain a CaCO₃ band in the 1450 cm⁻¹ and four bands at 800–1200 cm⁻¹, which slightly differ depending on the soil type. IR photoacoustic spectra of different soil types show much more distinct differences in the regions of 2950, 2520, 1900, and 1450–1500 cm⁻¹. In addition, the IR photoacoustic spectra of soils of the same type differ from each other less than the spectra of ATR modalities [170].

As discussed above, the correct sample preparation and methods are extremely important in molecular spectroscopy of soils. From the viewpoint of sample preparation, IR PAS also stands apart. Both ATR/ diffuse-reflection IR-spectroscopy and pressed samples for transmission IR modalities require samples with a particle size of less than ca. 100 μm (in fact, much finer grinding is required). But any grinding of soil leads to a serious mechanochemical changes in the molecular composition including changes in the phase composition (especially iron oxides), new surface groups in aluminosilicates, and the transformation of SOM itself. Otherwise, the contribution from specular reflection, especially for large particles should be taken into account [171].

Technically first were the papers based on laser-induced PAS of soils. E.g. a tuned CO laser-based (170 mW) IR PAS setup with a homemade cell (Fig. 4) and lock-in amplifier was used to determine the content of carbonate in soils (brown forest, chernozem, meadow soil, and marsh soil) differing in contents of SOM (0–50 %) and carbonate (0–40 %) by the weak characteristic band at 1800 cm⁻¹ [172]. The limit of detection (LOD) is 2 % (w/w) and the linear range is (0 ± 30) % w/w carbonate. In another study, a PLSR model shows the correlations between IR PAS spectra in the range 500–4000 cm⁻¹ and SOM, as well as nitrogen, phosphorus, and potassium available to plants [66,173]. The effectiveness of this approach is based on the severity of the photoacoustic effect in the case of SOM absorption [167], while the content of available nitrogen and phosphorus correlates with the content of SOM. Modeling the potassium content was not so successful as the photoacoustic effect is rather weakly expressed for compounds of this element. The same approach was used to determine labile carbon and showed the correlation of its concentration with the properties of bands of certain functional groups [159]. Similar strategies have been proposed for the determination of carbonate ion [160] and copper and sulfur [156]. Still these papers are based on a priori information on soil components and, even in multispectral modalities, cannot be used for complex SOM unknown. The effectiveness of such approaches is based on the contributions from inorganic matrix of soils. In the examples above, the major components were sulfate or carbonate species with relatively poor IR spectra. However, in the case of silicate soils (sodpodzolic, chernozems, etc.) the picture can be significantly different [174] making SOM analysis rather difficult.
The main results for FTIR-PAS are spectra of the soil as a whole or some of its components (mineral or organic) or fertilizers and using PAS for plant research and other objects [66,67,70,76,159,160,173,175,176]. The possibilities of PAS for assessing the distribution of a substance over the depth of microparticles are considered by examples of both model particles [103] and some soils [154]. The distribution of SOM along the depth of particle location in soil samples of the same field was studied (Fig. 5), which were selected between years of 1915 and 2011 [70]. The distribution of organic compounds in the soil particles is uneven, that or other functional groups occur at the depths that are characteristic for them. Based on the data obtained, conclusions were drawn on the effect of agricultural processes on SOM transformation.

Soil hydrophobicity is affected by SOM and soil water content [177,178]. FTIR-PAS was used for the investigation of reversible hydrophobicity of soils, i.e. the hydrophobicity that responds to water content. FTIR-PAS data show that, in response to hydration, surface molecules on wetted soil particles interacted differently with mid-IR radiation than surface molecules present in air-dried soils [68]. Authors claim that this results from reorienting amphiphilic molecules in response to hydration-driven entropic processes. These results suggest that FTIR-PAS can be used to elucidate how SOM and water interact at the molecular scale to drive soil hydrophobicity.

FTIR-PAS spectra revealed an absorption region in the wavenumber range of 1350–1500 cm⁻¹ that is claimed to be SOM and soil inorganic carbon near the surface (0–10 mm) of paddy soils dominated by C–O (carbonate) and C–H bending vibrations (organic materials), see Fig. 6. These vibrations were assumed as representing soil inorganic carbon and SOM, respectively [179]. Higher inorganic carbon content was observed near the soil surface, which, as authors believe, may play an important role in the soil carbon dynamics.

As soil particles are very heterogeneous in a microscopic scale, some modelling is required. Right now, this is under development and some simplified models are used. E.g. several papers are based on a simple model of a soil organic matter layer on the mineral core [69,154]. In the first paper, the possibilities of FTIR-PAS in situ depth-profiling of such systems were demonstrated on a complex film composed of a polyethylene preservative film and an office adhesive tape [69]. The depth-resolved information of such a complex film is derived by changing the moving velocity. The thickness of the cover tape estimated from PAS, 5.4–7.6 μm, is within the tape certificate thickness of 7 ± 1 μm. Spectral features of the polyethylene preservative film and office adhesive tape were extracted from the photoacoustic spectra of the heterogeneous complex film by means of independent component analysis [69]. On the basis of this paper, several studies by FTIR-PAS depth profiling at micrometer scales were made [154]. The compositional and structural differences in SOM (Fluvo-aquic soil, red soil, and chernozem) were explored from the surface to a depth of about 4 μm, see Fig. 7. The discriminatory power of principal component analysis of the soil spectra decreased with the reduction of scanning depths. The results showed that the distribution of potential hydrophobic cation-exchange capacity and SOM contribution to this value are different depending on types of soils, and most differences among the selected soil types occurred in the inner layer [154]. Correlations between soil properties and spectral absorbance were carried out to determine the source of water-extractable organic carbon, which significantly and positively correlated to the band intensity at 2920 cm⁻¹ for the black soil and significantly and negatively correlated with the band intensity at 1650 cm⁻¹ for the red soil. The authors claim that the black soil, in comparison with the red soil, has more contributions to water-extractable organic carbon from SOM [154]. However, the recent paper on chernozem soils shows that the majority of contributions in PAS spectra are from inorganic constituents, both fundamental lattice vibrations and overtone and combination modes of quartz and silicates.
For IR PAS (alike all methods of IR spectroscopy of soils), there is an important aspect related to the processing of spectral information. As IR spectra of soils represent all the soil components, on the one hand, it is important to extract the information pertaining to each component. On the other hand, it is necessary to recognize and distinguish spectral interferences from spectral changes caused by the interactions of components of organomineral complexes of organic matter itself. Differentiation of the obtained spectra makes it possible to improve the resolution of the bands, which is especially important when studying complex spectra of soils in which there are many sharp and few wide bands; differentiation allows choosing a suitable line [104].

Also, in several papers, chemometric approaches were developed for soil analysis. Most widespread are multivariate calibrations, and generalized and self-adaptive models for integral soil parameters [65,66,157,159,173,180]. FTIR-PAS with least square-support vector machine regression approach was then applied as a non-destructive technique to rapidly predict soil quality [156]. As we mentioned above, soil C and N can be predicted accurately whilst other components (P, K, Mg, Ca, and S), with the maximum ratio of performance to deviation of 2. Thus, FTIR-PAS may serve in real-time monitoring of soil quality and fertility. Based on FTIR-PAS measurements of 600 soil samples, a so-called optimal self-adaptive partial least squares model was proposed to predict SOM [65]. Classification of soils is carried out using the method of main components, and the proportion of correctly identified samples in the control sample is usually more than 95 % [181,182]. Still, this relevant area of IR PAS chemometrics is under development and requires appropriate methods of mathematical processing, which has not been developed in full yet. Authors of [183] used FTIR-PAS spectra together with $^{13}$C NMR to distinguish the organic components and make qualitative classification of organic and inorganic components based on mineral and organic peaks, although no quantitative comparison was made.

Step-scan FTIR-PAS was used for in situ elucidating the molecular composition of different regions of an oil shale (Green River, Colorado, USA) [59]. More than 30 characteristic DOM bands including aromatic and polyaromatic vibrations in the range of 3800–3600 cm$^{-1}$ were found throughout the whole set of oil-shale samples. Changes between layers in the oil shale at a micrometer scale were found by FTIR-PAS depth profiling. It was found that light-colored shale regions have a high DOM content, with spectra similar to that from isolated DOM, whereas dark-colored areas contain more mineral contents (clay minerals, montmorillonite, dolomite, calcite, and pyrite) by the set of bands assigned to CO$_3$, Al–O/Al–OH, Al–FeOH, Si–O, Al–O–Si, and Si–O–Fe [59]. Rather important are band shifts in DOM spectra in the shale samples compared to spectra of isolated DOM. This suggests considerable non-covalent interactions between DOM and mineral components.

To summarize this section, the application of all methods of IR PAS of soil to-date are diverse but mainly limited to basic soil composition, the total SOM, the texture and mineralogy of clay minerals, the availability of nutrients and the evaluation of certain other properties (fertility, structurization, bacteriological activity). It is assumed that IR-spectroscopic properties of the soil can be interpreted as an...
Fig. 5. Depth profiling by PAS of a soil sample collected from a Tucker Prairie (native prairie that has never been cultivated) and plot 2 at Sanborn Field in year of 1915. Each frequency represents a different profiling depth. Plot 2 has been planted to wheat and amended with an inorganic fertilizer since 1888 [70].

Fig. 6. FTIR-PAS spectra of paddy soils (n = 739) collected with a moving mirror velocity of 0.64 cm s\(^{-1}\). The shaded frame shows the absorption band in the wavenumber region of 1350–1500 cm\(^{-1}\). doi:10.1371/journal.pone.0043368.g001 [179].

independent indicator, which may provide new outlooks on soil analysis and research, but this task has not yet been solved. A complete structural and functional analysis, fractional analysis, and the expansion of IR photoacoustic measurements in the far and near IR regions are also not done yet in full.

5. In situ photothermal microspectroscopy and hyperspectral microimaging of soils and rocks

State-of-the-art photothermal microscopy and imaging techniques provide high-resolution spectra with high sensitivity and locality. Still, all optical/IR techniques obey the limitation of the diffraction limit as microspectroscopy techniques. Thus, the information regarding the heterogeneity of DOM chemical composition at the nanoscale is lacking. Another aspect of this problem is that in situ measurements of the chemical composition and physical and mechanical properties of DOM help understanding the formation, transformation, and utilization of organic matter in soils as well as rocks and shale. These problems are being challenged by photothermal probe microspectroscopy (or photothermal induced resonance, PTIR).

Indeed, despite the name, photothermal microspectroscopy is comprised by the methods rather different from both absorption (micro)spectroscopy and other methods of photothermal spectroscopy mentioned above (PBDS and thermal-mirror techniques) — in fact they belong to probe microscopy. These methods use the cantilever-based probes of thermal microscopic techniques (like atomic-force microscopy (AFM); scanning thermal microscopy (SThM), and scanning near-field optical microscopy (SNOM) [184–189]. Photothermal probe microspectroscopy is based on the detection of the transient and local dilatation of a sample upon resonance heating by a lamp, IR source, or, preferably, a (tunable) laser. Laser sources, like CO\(_2\) lasers [190,191] or, more recently, QCL lasers, serve as main excitation sources in PTIR. Synchrotron IR radiation sources are also used to improve the quality of the spectra [192,193]. The absorption of a source pulse in the sample results in local heating, sample local expansion (photothermal signal), and the excitation of the deflection or motion of a high-frequency cantilever [194–196]. The cantilever deflection is used to measure the forces between the probe tip and the sample and thus to map the topography with a nanoscale lateral resolution [194,195,197].

Photothermal induced IR resonance (or atomic force microscopy-based IR spectroscopy, AFM-IR) is one of most widespread of such methods [198,199]. This method measures the transient thermal expansion induced by pulsed IR absorption in the sample with an AFM tip in a contact mode. Samples placed on a transparent prism are illuminated in a total-internal reflection modality to minimize the direct interaction of the excitation beam with the AFM tip (Fig. 8).

The advancement of this technique is peak-force IR microscopy (PFIR) [200,201]. In this technique, frequency-tunable QCL IR laser pulses are guided to the probe tip and sample region of an AFM operated in the PeakForce Tapping AFM imaging mode (technology by Bruker Inc.), see Fig. 9. This mode operates at rather low frequencies of 1 or 2 kHz and allows a controlled tip-sample contact; laser pulses are synchronized with every other peak force tapping cycle [201]. The IR radiation absorption by the sample leads to volume thermal expansion capable of excitation of the contact resonance of the cantilever. The expanded volume persists for a certain time before returning to the initial value due to heat dissipation through thermal conduction with the surroundings. The position sensor records these time-resolved vertical deflections of the cantilever with and without the laser pulse. Their difference provides a PFIR trace that carries the change of the cantilever motion due to photothermal excitation of the sample. According to [201–203], a PFIR trace contains three parameters representing the laser-induced effects: (i) the excitation of the contact resonance, (ii) the baseline offset of the PFIR trace that represents the expanded volume due to thermal expansion, and (iii) the change of the slope of the baseline of the PFIR trace after the pulse related to the rate of thermal dissipation through local thermal conductivity or possible changes of modulus after IR absorption. Like other PTIR techniques, Fourier transform is used to extract the amplitude of the contact resonance oscillation that is proportional to the local IR absorption.

As these techniques are based on the tip size rather than the IR wavelengths, they make it possible to obtain IR spectra with a
resolution of down to 20–30 nm or better, which is a significant enhancement relative to techniques of condensed-phase IR spectroscopy. PFIR provides a < 10 nm spatial resolution [201]. It is important that the spatial resolution does not depend on the wavelength of the source radiation, but only on the dimensions of the probe and thermal properties of the sample. Also, the resolution depends on the thermal conductivity of the probe and contact area of the probe and sample.

Key features of PTIR are the same as common IR techniques: sample preparation is minimal or absent, the technique is nondestructive, and is capable for spectroscopic measurements of a variety of analyzed objects including heterogeneous specimens. This advantage is beneficial over e.g. Rock-Eval pyrolysis, which requires the sample to be heated to hundreds of degrees centigrade to characterize the chemical composition. As a microspectroscopic technique, PTIR modalities provide imaging, and the resolution is higher than for conventional techniques of FTIR spectroscopy (although not for all the samples and a further increase in the spatial resolution is awaited). The advantages of PTIR resulted in its implementation in commercially available tabletop instruments produced by Bruker, which are used in many applied studies [204,205], and a focused overview of the use of PTIR in interface and materials science is published [206].

PTIR is able to handle inhomogeneous samples with simultaneous mapping of both inorganic and organic matrix in solid samples of a submicrometer scale, with a spatial resolution around the tens of nanometers [207]. It also inherits the advantages of photothermal spectroscopy, the possibility of determining small amounts of matter. PTIR spectra depend on the absorption coefficient and similar to the reversed traditional absorption IR spectra and, hence, are directly comparable with FT-IR spectral libraries [208,209]. Alike in PAS, changes in PTIR spectra compared to conventional modalities relate to thermal factors, the formation and propagation of thermal waves. Photothermal spectra may reflect the photothermal saturation due to violation of the linear dependence between the signal and high values of the absorption coefficient. This results in the peak suppression [209].

In the case of DOM, PTIR was used to measure the chemical and mechanical nanoscale heterogeneities in oil shale [210]. The results document the evolution of individual organic macerals (strongly aromatic inertinite [strong C–H absorbance aromatic C=C ring stretching absorbance bands at 3000–3100 and 1600 cm⁻¹, respectively and relatively low oxygenated group stretching at 1710 cm⁻¹], solid bitumen [no band at 3000–3100 cm⁻¹, modest at 1600 cm⁻¹, and modest C=O stretching at ~1710 cm⁻¹], and tasmanites [intense C=O absorption at ~1710 cm⁻¹ and low aromatic absorption at 1600 cm⁻¹]) of the shale with maturation, providing a microscopic picture of the heterogeneous processes of petroleum generation, Fig. 10 [210].

PTIR is also used to map the mechanical moduli in source rocks as a conglomerate of inorganic minerals (i.e. silicates and carbonates) interspersed with finely distributed organic matter (Fig. 11) consisting mainly of SOM at the nanoscale [211] and to determine differences between the components [212]. Authors claim that distinguishing the organic and inorganic phases may explain how nanoscale properties influence the macroscale moduli measured from bulk rock samples. As the continuation of this study, peak force IR microscopy was used for multimodal characterization of SOM in organic shales [200].

Fig. 7. Mean difference spectra between each pair of three soil types for different moving-mirror velocities. Significance of differences (Tukey HSD multiple comparison test, α = 0.01) at each wavenumber is presented in solid lines [154].
provided correlative IR imaging, mechanical mapping, and broadband IR spectroscopy capabilities with a 6-nm spatial resolution within the region of 2400–4000 cm\(^{-1}\). The authors claim assessing nanoscale heterogeneity in the chemical composition, aromaticity, and the level of maturity of the SOMs from source rocks. The level of aromaticity of the SOM positively correlates with the local mechanical moduli of the surrounding inorganic matrix, offering insights into the effect of SOM heterogeneity on the nanoscale mechanical properties of the source rock.

6. Other soil component analysis by photoacoustic and photothermal techniques

6.1. Gas and soil headspace analysis

FTIR-PAS is used for the gases volatilized from soils. The main idea of these studies is that gas concentration in soil headspace is directly linked to its volatilization. An important task is nitrogen loss in soils depending on the soil type and nitrogen fertilization, mainly as nitrous oxide (N\(_2\)O) and ammonia (NH\(_3\)), the latter is a major pathway of nitrogen loss in alkaline soils. Ammonia from alkaline soils was characterized by FTIR-PAS using two absorption bands at 850–1200 cm\(^{-1}\), Fig. 12 [158]. For three treatments (a control without nitrogen compounds added, urea, and coated urea), NH\(_3\) concentration in the incubation and pot experiments could not be directly used to model the NH\(_3\) emission in field experiments due to the differences in fertilization processes and application rates as well as soil temperature and specimen disturbance [158]. Another study is connected with the monitoring of nitrogen volatilization from different types of fertilizers [155]. FTIR-PAS with a non-static, non-flow-through chamber for gas collection and analysis was used. N\(_2\)O and NH\(_3\) emissions from polymer-coated urea as a controlled-release fertilizer and conventional uncoated urea were compared for sand, sandy loam, and loam soils for short-term and full-term studies. The results of 20- and 45-day experiments showed that polymer-coated urea decreased gaseous losses of nitrogen following fertilization while providing a steady nitrogen supply to plants. Authors highlighted that FTIR-PAS provided a higher time resolution compared to other instruments [155]. Thus, high sensitivity of PAS and high selectivity of FTIR provide rather high precision of measurements for decision-making.

A PAS setup with cw CO\(_2\) laser excitation and a non-resonant (uniform pressure rise) cell at high temperatures was used to assess total organic carbon (TOC) in soil aqueous solutions by determining dissolved CO\(_2\) under the conditions of a standard TOC procedure. For such a cell construction and low absorptivities, the peak height is directly proportional to the absorbance and the analyte concentration. LOD of 4 mmol L\(^{-1}\) was achieved at a cell temperature of 775 K with a rather good precision of assessment [213].

6.2. Soil solution analysis

Most of informative analysis methods of complex mixtures (liquid and gas chromatography coupled with various detection methods like mass spectrometry or liquid NMR spectroscopy) require solutions. Both PAS and PTS can be implemented with the majority of the state-of-the-art separation techniques as highly sensitive detectors [57,214,215]. Until recently, the majority of application of PAS in soil solutions was focused on low molecular-weight organic compounds due to its huge importance for petroleum exploration and oil geochemistry [216].

Some studies dealing with soil solutions are focused on single-element analysis either due to characteristic bands of their small-molecule compounds (usually, decomposition products) or by formed colored compounds. Well-known photometric reactions are used in photothermal spectroscopy for high-sensitivity measurements [57]. E.g., phosphorus heteropoly molybdate reaction was used to assess orthophosphate in soil solutions using collinear PBDS with a cw
Fig. 9. Operational scheme of PFIR microscopy: (A) operation diagram for the PFIR apparatus; (B) gate-averaged traces of vertical deflections of the cantilever with the laser interaction (red curve) and without the laser interaction (blue curve). The timing of the IR laser pulse (black curve) is selected to be within the contact regime of the peak-force tapping cycle. Subtraction of the two vertical deflection traces is used to obtain the PFIR trace [201].

Fig. 10. Nanoscale geochemical and geomechanical characterization. Inertinite (a), solid bitumen (b), and Tasmanites (c) in stiffness images are identified by comparison with a photomicrograph of the same field. Areas outside of regions of interest are masked with opaque color to screen out irrelevant contact resonance frequency measurements. Contact resonance frequency histogram for 130.74 μm² area of inertinite (d), 272.97 μm² area of solid bitumen (e), and 201.67 μm² area of Tasmanites (f). Localized IR spectra from different locations (colored points in corresponding stiffness images) in inertinite (g), solid bitumen (h), and Tasmanites (i) [210].
with separation techniques. The determination of nonphosphate has been achieved.

The spectra can be used to distinguish quartz (green band) (d) from organic matter (red band) (e) [212].

A semiconductor diode laser at 790 nm [217]. LOD of 0.1 \(\mu\)mol dm\(^{-3}\) of phosphate has been achieved.

The capabilities of high-sensitive PTS measurements are used also with separation techniques. The determination of nonfluorescent nitroaromatic explosives in a contaminated soil of a near-field thermal lens detector in the deep UV region (excitation beam, 257 nm) for micellar electrokinetic chromatography was proposed [218]. These compounds are detected with LODs that are 1–2 orders of magnitude lower than those obtained with transmission spectrometric detection.

7. Thermal parameters of soils

Thermal properties of soil is another area of application of PAS and PTS. Determination of thermal diffusivity of soils and the assessment of the degree of influence of such factors as moisture content, particle size, and mineralogical composition, as well as organic matter content, are topical tasks of soil science [219–222]. Commonly, experimental assessment of thermal parameters of soil is carried out for either in situ or with very large samples by direct temperature measurements, or under the conditions of destructive lysimetric experiments. Computational models for thermal properties of soils are also retrieved from bulk component materials and large soil samples [219,223]. PTS and PAS make it possible to assess the thermal diffusivity of soils with high locality and without sample decomposition. Despite its use in several neighboring fields, photothermal spectroscopy and imaging is not yet commonly used in investigations of temperature-related problems in soils, but there are new findings in this area.

IR thermal imaging under controlled laboratory conditions provides an approach to determining the thermal diffusivity of soils [224]. Subject to one-dimensional heat flow conditions, an axial heat flow method is used to back-calculate the soil thermal diffusivity. The method has been applied on four compacted samples of kaolin soil under transient conditions with satisfactory agreement between the experimental and calculated data [224].

Another approach is based on photothermal beam-deflection spectroscopy. This method was used for assessing thermal diffusivities of several types of soil and individual soil aggregates (2 × 2 mm) [121]. PBDS distinguishes between thermal diffusivities of different soil types: sod-podzolic, chernozem, and light chestnut soils. The precision of measurements was enough to differentiate thermal diffusivities of aggregates of chernozem for virgin and bare-fallow samples. For soil profile micromonoliths, PBDS is capable to distinguish thermal diffusivity values resulting from the changes in the structure of aggregates for different soil layers. It is claimed that PBDS can be used for studies of changes in properties of soil entities of different hierarchical levels under the action of agrogenesis [121].

Photothermal radiometry was used for assessing thermal properties of limestone (Fig. 13), which depend on the microstructure and organomineral composition. The effect of the thermal treatment from 100 to 600 °C of limestone rocks was studied. It is shown that the thermal diffusivity, thermal conductivity, and specific heat of limestone decrease with temperature, which can be accounted for by increased microcracks and effective porosity due to thermal treatments [63]. Photothermal radiometry was complemented by X-ray diffraction characterization and effective porosity measurements.

Thus, PTS can be used to find very important features of the sample like heat capacity and thermal diffusivity, and at local spots. The latter is especially important for heterogeneous objects, whereas the classical thermochemical methods can give the average characteristics of the sample only.

8. Conclusions

To sum up, the analysis of existing results of application of
photoacoustic and photothermal spectroscopies for soils and SOM draws the following conclusions.

(i) Due to state-of-the-art possibilities, photoacoustics of soil and SOM is more advanced compared to PTS. FTIR–PAS can be used to determine the main components of soil samples when the use of ATR or diffuse-reflection modalities is difficult or impossible. The existing applications of IR PAS are rather diverse, and most usual is qualitative characterization of major soil components, estimation of total SOM, SOM assessment with the estimation of clay minerals, and the evaluation of the availability of nutrients and certain other properties from PAS spectra as integral parameters.

(ii) Optical photoacoustic spectroscopy as well as IR PAS single-wave modalities are used in combination with other methods, mostly X-ray powder diffraction for mineral components of rocks and soil with SOM or its components as indirect results.

(iii) The possibilities of PAS for assessing the distribution of a substance over the depth of microparticles are considered on model particles and some soils, although the applicability of soil-particle models should be further advanced and evaluated.

(iv) The possibilities of nanometer-scale measurements (nanoscopy) of DOM in rocks and minerals using photothermal-probe modalities is shown and provides rather informative spectra implementing fluorescence and optical images with a superior resolution beating the diffraction limit.

(v) Photothermal beam-deflection spectroscopy and photothermal radiometry can be used for macroscale and microscale imaging of thermal diffusivity of soils.

As a whole, photoacoustic and photothermal spectroscopies in SOM research complement each other, while PAS is used mainly in multispectral or interferometric modalities for spectral characterization, photothermal methods are less frequent and mainly used for thermal parameters. However, the situation starts to change with the appearance of photothermal-probe methods, which provide rather reliable spectral information with a nanometer-scale spatial resolution. Despite the demonstrated research capabilities of the discussed methods, there are still significant gaps in their use with respect to soil objects:

(i) In the near IR region (due to a large number of hardly identifiable overtones and combination bands from SOM, aluminosilicates, and water) there are few scarce studies with PAS. There is not much studies on the use of PAS in the far IR region (it is true for all kinds of studies or organic matter, not only SOM). However, it is the use of the entire IR range that is extremely important for the understanding of complex organomineral systems such as DOM and SOM.

(ii) In our opinion, depth scanning of soil particles—the inherent feature of FTIR PAS—has not been implemented in full yet as it involves both the correct estimation of the penetration depth and appropriate models for soil particles. Especially important is step-scan FTIR PAS with the constant penetration depth for the whole spectral range. It is this feature that makes this method a key for studying depth distribution of SOM and inorganic matter in particles and aggregates, which is not currently available in full.

(iii) There is little data in the combination of soil fractionation and PAS investigation of individual soil fractions [174], although the possibilities of the optical and IR modalities of PAS should be manifested here most fully because of characteristic changes in the composition of soil particles with size and structure [225–227].

(iv) There are no studies in which IR PAS spectroscopy is used as a full-scale method of quantitative structural (molecular) or functional analysis.

(v) It is assumed that IR PAS features can be interpreted as an independent indicator of the soil properties, which may provide new outlooks on soil analysis and research, but this task has not been solved yet.

(vi) IR PAS chemometric models are quite important for the progress in this field and are under development, but more appropriate methods of post-measurements processing are still required despite their successful use in PAS of various samples [72].

(vii) Photothermal microspectroscopy requires a more developed methodology for soils, especially for its components at microscale levels like microaggregates, etc.

Thus, in general, along with significant success in the analytical capabilities of photoacoustic and photothermal methods for soils and SOM, the task of developing a methodology for integrated analysis and diagnostics with reference to systems of such complexity is very relevant still. In our opinion, the situation should follow the routes of proteomics and metabolomics that are now leading (or have already led perhaps) to the new methodology of ‘omics’ and an explosive bloom of methods in these areas. However, the task of establishing the structure of SOM (and DOM as a more general problem) is much more complicated than the same problem for biomacromolecules, which is why it is unresolved until now.

To advance here, significant progress is needed in the field of instrumental applied chemistry determining the limits of applicability of various approaches and the development of hyphenated methods of analysis and algorithms for information processing. This implies both new methods of complex diagnostics combining physical tests and chemical analysis, as well as metrological assurance of measurements and further development of methods for processing the spectral information. Considering the existing results and the progress in the development of photoacoustic and photothermal methods, they will play
an important part in the nearest future.

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