APPLICATION OF FOURIER-TRANSFORM INFRARED SPECTROSCOPY FOR QUANTIFICATION OF CHEMICAL PARAMETERS IN PEAT SAMPLES

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Abstract. The demand for the characterization of soil properties on a wide geographical scale with a high spatial resolution is constantly growing to implement various competitive studies, including climate and ecology studies. However, conventional soil analysis methods are time-consuming and expensive. Fourier-transform infrared spectroscopy (FTIR) has the potential to provide an alternative solution for the rapid and cost-effective determination of soil chemical and physical parameters. In this study, we calibrated a mid-infrared diffuse reflectance Fourier transform spectrometer (MIR-DRIFTS) for the determination of commonly analysed soil parameters such as pH, carbon (C), nitrogen (N), phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K) and humic acid content and evaluated the performance of the elaborated soil analysis MIR-DRIFTS methods. The spectrometer calibration was performed by partial least squares regression analysis using soil spectra data acquired by the spectrometer and soil parameter reference values for the same samples acquired by traditional soil analysis methods. For calibration and validation of the MIR-DRIFTS methods, soil spectra were acquired in 3 replicates for a total of 1891 peat and peaty soils. To evaluate the performance of the elaborated MIR-DRIFTS methods, their uncertainty was evaluated by estimating the precision and accuracy of the results obtained. The highest potential of MIR-DRIFTS performance was observed for the determination of pH, C, N, and humic acid content, with an estimated combined uncertainty ranging around 6%, 6-28%, 16-20%, and 26-50%, respectively, depending on the analyte concentration. The estimated combined uncertainty of Ca, P, Mg, and K concentrations determined by MIR-DRIFTS ranged from 28-49%, 34-37%, 33-57%, and 57-100%, respectively. It was observed that the MIR-DRIFTS method's performance is highly sensitive to the availability of samples used for method calibration. An increased number and diversity of samples used for calibration can improve the performance of MIR-DRIFTS methods of soil parameter determination.

Keywords: FTIR, diffuse reflectance, soil spectroscopy.

Introduction

Growing requirements of sustainable soil management highlight the need for high-resolution spatially explicit information on soil resources. As a result, there is an increasing demand for soil analysis in fields such as climate and ecology studies, as well as sectors related to soil management. However, traditional soil analysis methods are labour-intensive, time-consuming, and require significant financial resources to analyse large quantities of soil samples. Therefore, the relevance of soil spectrometry methods as a cost-effective alternative for bulk sample testing is gaining attention. FTIR spectrometry is an analytical technique that measures the absorption of infrared light by chemical bonds in a sample. The resulting spectrum showing absorption at each wavelength or wave-number reflects the chemical bonds present in the sample and provides information to simultaneously predict multiple properties of the sample. FTIR has applications across various industries, including forensics, biological and medical applications, material science, production quality control and environmental sample analysis, including soil analysis.

Previous studies have demonstrated that FTIR spectrometry can be used to quantify the chemical composition of both soil organic and mineral matter [1-6]. Extensive soil spectroscopy studies carried out by comparing results obtained by traditional soil analyses and FTIR methods of more than 53 000 samples have provided evidence that soil spectroscopy has high potential to provide a solution of rapid, high-throughput soil chemical analysis solution [7-13]. These studies used mid-infrared diffuse reflectance Fourier transform infrared spectrometer (MIR-DRIFTS) equipped with an autosampler, therefore it has even higher sample throughput compared to other MIR-FTIR spectra acquiring techniques such as by transmission or attenuated total reflection.

One major drawback of FTIR methods is the initial investment required to calibrate the soil chemical parameter prediction methods, as well as the challenges in transferring the developed calibration to other FTIR instruments [10; 11] and applying it to soil testing from different regions. To develop a robust method, the calibration sample set should be as diverse as possible and fully represent the target samples to be tested [14]. However, even calibrations developed for local application may not

provide optimal performance due to a limited library of spectra used in the calibration, considering the diversity of soils available. Attempts to apply such calibrations to soil from a wider region may further reduce the performance of the method. Another limiting factor for the widespread application of the method is the technical parameters of the spectrometers, such as the IR light frequency range and resolution, as well as the variety of spectrum acquisition techniques (diffuse reflectance, transmission ATR), which pose challenges in sharing the developed calibrations.

Therefore, there is still a need for standardization and validation of FTIR application in routine analysis across different laboratories and research groups which prioritize the creation of locally representative standardized spectral laboratories aiming to establish harmonized spectroscopy methods with wide inter-comparable application [15; 16]. The current spectral libraries mainly consist of information from samples of mineral soil and therefore cannot be easily used for organic soils. The objective of this research was to initiate a development of a spectral database for organic soils, including peat, and to establish preliminary calibration models to assess the capability of the method in predicting various properties such as acidity (pH), total carbon (C) and nitrogen (N), nitric acid extractable phosphorus (P), calcium (Ca), magnesium (Mg), potassium (K), and humic acid content in peat samples.

Materials and methods

This study used MIR-DRIFTS spectrometer Bruker Invenio-S equipped with an HTS-XT accessory allowing rapid measurements of dried and homogenized samples. To calibrate and validate models for predicting soil chemical parameters, soil samples were chosen from peatlands with different land uses, as well as undrained and drained forest stands with peat soil and varying forest site types. Samples were collected from a soil at depths up to 80 cm. Most of the sample set consisted of organic soils, with a few exceptions of mineral soil from deeper soil layers.

The peat samples were air-dried and milled into a fine powder. The air-dry organic soil samples, which may have contained mineral particles, were homogenized and then passed through a 2 mm sieve. Three spectral replicates were obtained for each of the 1891 samples, resulting in a total of 5673 acquired spectra. A separate subsample was used for each measurement replicate. Reference values for soil parameters calibrated (pH, C, N, P, Ca, Mg, K and humic acid content) were acquired in ISO 17025 accredited laboratory by using ISO standard methods for all parameters, except for humic acid content, which was determined using a national testing method. Humic acid was also an exemption regarding the availability of reference values, as those were available for 100 samples only.

To elaborate the FTIR methods, a chemometric calibration model's development was based on multivariate analysis using the partial least squares (PLS) regression method integrated into the Bruker OPUS software. This was done by using the acquired spectra of the calibration and validation set of samples and the reference values of the chemical properties of the samples. The proportion of calibration and validation samples was 70% and 30%, respectively. A PLS algorithm by Bruker ensured that the appropriate principal components or factors of the spectral data matrix were utilized during calibration to establish the strongest correlation between the spectral and the reference data of the soil chemical properties. Multiple versions of calibration models were developed for each soil parameter that was calibrated. The versions were created based on whether data extremes were included, the choice of spectrum pre-processing methods, and the selection of different spectral regions. The calibration approach for each version was determined by the quality indicators obtained from cross-validation, which was performed using the calibration sample set. The quality indicators included coefficient of determination (R^2), root mean square error of cross-validation (RMSECV), residual prediction deviation (RPD) and a number of calibration factors used by the model.

The calibration models created were validated by predicting the chemical composition of validation samples set by using their infrared spectra and created versions of the calibrations. The prediction results of the model version with the highest quality for each soil parameter, as provided by the validation procedure, were selected for evaluating the uncertainty of FTIR prediction methods. The uncertainty was calculated according to the Nordtest approach by combining the relative standard deviation (RSD) and bias of predicted soil parameter values [17], which represent both the accuracy and precision of the method. Calculation of the uncertainty of FTIR prediction also considered the uncertainty of reference methods performed by the respective laboratory.

Results and discussion

Values predicted by elaborated MIR-DRIFTS calibration models show high correlation (r from 0.92 to 0.99) with the reference values of C, N, P, Ca, Mg and pH determined by ISO standard methods (Fig 1). Correlation coefficients for values of K and humic acid are 0.75 and 0.66, respectively. However, while reference values of humic acid were available for 100 samples only, MIR-DRIFTS performance of humic acid content prediction in peat samples can be considered with high potential as demonstrated by the relationship between predicted and reference values as shown in Fig. 1. It cannot be excluded that few excessive outliers affecting coefficient of determination were errors in the reference values.
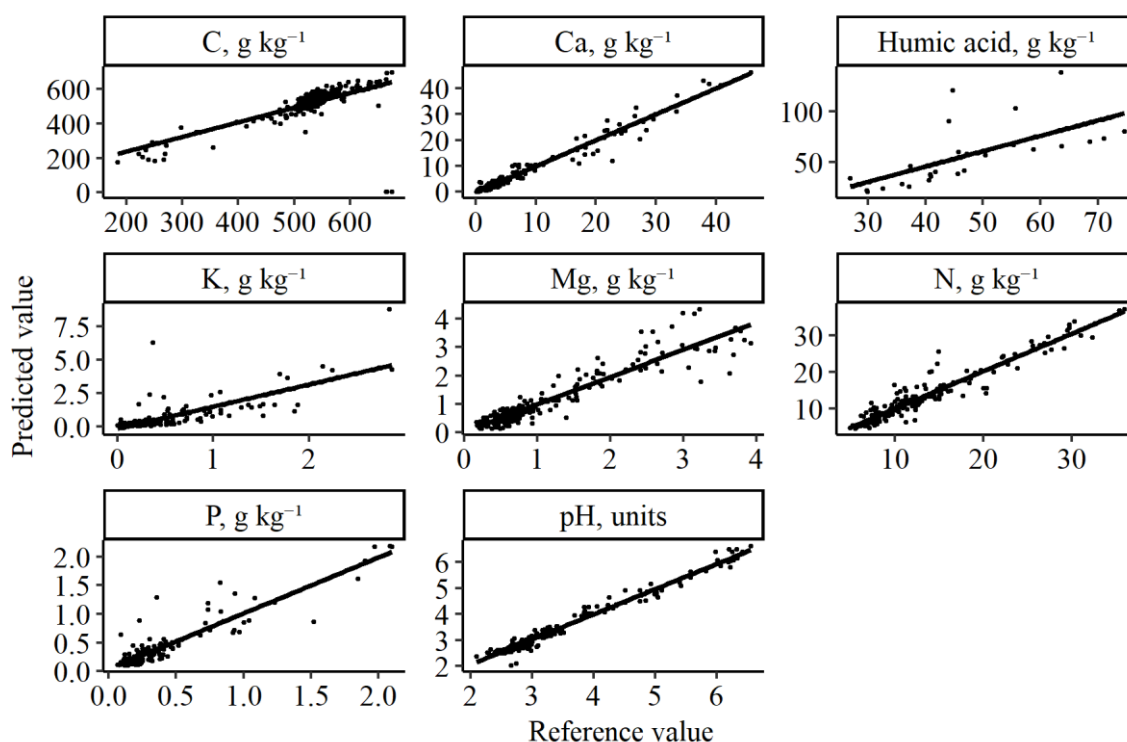

Fig. 1. **Relationship between predicted and reference values of the analyte concentration**

RPD not exceeding values around 1.4 to 2 (calculated as a ratio of standard deviation to prediction error) is a commonly used threshold that indicates it may be difficult to apply the FTIR method for predicting the quantity of an analyte in unknown soil samples [18]. In our case, other quality indicators acquired by validation of elaborated methods according to the Nordtest approach did not always agree with the assessment of the FTIR method's potential to predict a chemical composition of unknown soil samples by RPD value alone. According to the RPD values acquired, pH, Ca, and Mg have the best potential for accurate prediction, while P and K have the lowest potential. However, the acquired values of root mean square bias of predicted values from reference values as well as the relative standard deviation of C, N measurement result replicates tend to be even lower compared Ca and Mg with higher RPD ratio (Table 1). Results of the validation procedure show that combined uncertainty of pH prediction is 6% while depending on the analyte concentration, uncertainty of C and N concentration prediction ranges from 6 to 28% and from 16 to 20%, accordingly. While the uncertainty of Ca and Mg prediction results was between 28 to 57%. For comparison, the range of estimated uncertainty of methods used for the determination of references values is from 1.7 to 13.4% for pH and P, respectively. Comparably poor prediction of P (combined uncertainty from 34 to 37%) was likely introduced by narrow concentration range represented by the calibration and validation sample set, as only a relatively small number of samples had P concentration above 0.5 g·kg⁻¹. The worst performance was acquired for the prediction of K, which also had a narrow concentration range represented by the reference values of the samples available. However, K has proven to be a problematic element to be quantitatively determined also by previous studies [10].

Table 1

Results of the calibration model's validation

Parameter	Concentration range	RPD	Bias, %	RSD, %	Combined uncertainty, %
pH	pH 2.0-6.6	6.28	5.5	1.5	6.2
C	33.7-540.0 g·kg^{-1}	2.6	26.1	10.4	28.1
	540.0-699.0 g·kg^{-1}	1.53	5.9	1.2	6.3
N	4.4-13.0 g·kg^{-1}	1.62	19.2	5.1	20.1
	13.0-37.4 g·kg^{-1}	2.35	14.4	5.3	15.8
P	0.1-0.6 g·kg^{-1}	1.63	33.6	9.33	36.9
	0.6-2.2 g·kg^{-1}	1.28	27.9	13.0	33.6
Ca	0.3.0-10.0 g·kg^{-1}	2.15	46.4	9.4	48.6
	10.0-47.0 g·kg^{-1}	2.05	24.8	6.9	27.5
Mg	0.1-2.4 g·kg^{-1}	2.67	55.4	12.3	57.3
	2.4-4.4 g·kg^{-1}	2.1	31,4	4.2	32.7
K	0.005-1.7 g·kg^{-1}	1.62	100.0	16.8	102.0
	1.7-8.8 g·kg^{-1}	1.18	66.3	7.8	67.6
Humic acid	20.9-85.0 g·kg^{-1}	1.99	22.5	8.3	26.0
	85.0-138.6 g·kg^{-1}	1.23	50.2	8.8	52.0

Experience of other studies shows that likely the number and variety of calibration samples and measurement replicates would contribute to further reduction of prediction uncertainty. While this may be a solution for other analytes, in our study we noticed that adding peaty soil samples with lower C concentration to the calibration data set did not improve the model's performance. However, this was likely an effect of samples with mineral soil particles that may have introduced bias in the calibration. Using only peat soil calibration data set with similar spectra selected by PCA had the best prediction performance. As a result, we conclude that caution should be taken during a selection of the sample set for calibration. While, in general, a higher diversity of samples increases the robustness of the method, introduction of samples with mineral particles may introduce errors in models aimed at prediction of chemical composition in peat samples specifically. In case of significant differences in the sample matrix, it is recommended to create separate calibration models based on spectra sets selected by PCA results and apply these models to unknown samples based on spectral residues and Mahalanobis distance. However, if the calibration data set is insufficient, further division of it by PCA results may not always improve model quality due to an insufficient number of spectra in different batches. Also, other studies recommend caution when expanding a spectral library to ensure that it does not become too diverse as an excessively diverse sample library can result in poor prediction outcomes [19]. Procedures performed showed that elaboration of prediction models aimed at specific soils, in our case peat, could be hampered if a limited number of samples with known reference values does not provide representativeness of a wide concentration range of the analytes of interest.

By evaluating bias and RSD of prediction results we noticed that the performance of MIR-DRIFTS methods may be enhanced by improving the sample preparation procedure to ensure more homogenous samples. The quality of the spectra can be affected by the milling process, which can introduce noise and artefacts. Finer milled samples could provide higher-quality spectra as the fine particle size ensures that the sample is homogenous and sample representative [20]. Acquiring sample spectra in three replicates often resulted in RSD pf predicted soil properties exceeding 10%. The choice of performing sample testing in five replicates would allow for discarding highly deviating results and could potentially reduce the uncertainty of the prediction. It should be also taken into account that errors of predicted soil chemical properties concentration values depend not only on the quality of the acquired spectra but also on the accuracy of the reference values used in calibration. In our study uncertainty of the reference methods is included in the estimation of the combined uncertainty of the elaborated MIR-DRIFTS methods.

Conclusions

1. MIR-DRIFTS provided excellent performance (RPD ratio of 6.3) of pH prediction in soil with uncertainty of 6%.
2. Prediction results of C, N, Ca and Mg are promising (RPD ratio from 1.5 to 2.7) as a higher number of reference samples representing a wider range of analyte concentration would likely contribute to further reduction of result uncertainty. The same applies to the prediction of humic acid concentration whose performance was affected due to a small number of samples with reference values available.
3. For further improvements of the MIR-DRIFTS spectra library, scanning of samples in five replicates is recommended.

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Author contributions

Conceptualization and methodology, A.B., spectra acquiring, Z.A.Z., calibration and validation, A.B. and Z.A.Z; writing – original draft preparation, A.B and Z.A.Z., writing – review and editing, A.B and Z.A.Z. All authors have read and agreed to the published version of the manuscript.

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