
Handheld Near-Infrared Spectrometers: On-Site Quality Control and Protection Against Product Counterfeiting

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Abstract

Recently, miniaturization of vibrational spectrometers (Raman, mid-infrared (MIR) and near infrared (NIR)) has made substantial progress, and marketing companies predict this segment of instrumentation a significant growth rate within the next few years. This increase will be based on a wider adoption of spectrometers for quality control by in-the-field testing and on-site measurements. Furthermore, based on high-volume manufacturability and significant reduction of costs, numerous companies target with handheld NIR scanners a non-expert user community for consumer applications. Especially from this last-mentioned development, a tremendous potential for everyday life can be expected, ranging from food testing to detection of fraud and adulteration in a broad area of materials. The present communication focuses on the building principles of state-of-the-art handheld NIR instruments, and will discuss selected applications such as quality control of peony oil, authentication of cotton/silk textiles and the use for bauxite exploration, in order to demonstrate the diversity of their applications.

Keywords: Handheld NIR spectroscopy, Quality control applications, Peony oil, Cotton/silk textiles, and Bauxite exploration.

1. Introduction

Miniaturization of vibrational spectrometers has started already at the end of the last century, but only within the last two decades real handheld Raman, MIR and NIR scanning spectrometers have become commercially available, and utilized for a broad range of analytical applications (1 - 6). In Fig. 1 selected examples of handheld spectrometers for each of the three techniques are shown.



While the weight of the majority of Raman and MIR spectrometers is still in the ~1 kg range or higher, the miniaturization of NIR spectrometers has advanced down to the ~100 g level, and developments are under way to integrate them into mobile phones (7). Furthermore, Raman and MIR handheld spectrometers are still in the price range of several tens of thousands of US\$, because despite miniaturization they offer a multiplicity of accessories, such as orbital raster scanning (ORS) and surface-enhanced spectroscopy (SERS) for the Raman technique and different measurement modes for Fourier-Transform IR (FT-IR), such as attenuated total reflection (ATR) and diffuse/regular reflection. In contrast, miniaturized NIR systems have recently reached the < \$1,000 USD level and in the near future, only the acquisition of NIR systems can be taken into consideration for private use. Therefore, handheld Raman and MIR spectrometers will be restricted to industrial, military, and homeland security applications, as well as public use by first responders, customs, or environmental institutions.

Near-infrared (NIR) spectroscopy is primarily based on absorption bands of overtone and combination vibrations of C-H, O-H, N-H, C=O, and C=C functionalities (8) and, in combination with chemometric evaluation methods, has proven to be an excellent tool for qualitative and quantitative analysis (9). Due to the comparable chemical specificity and simplicity of sample measurements and the abovementioned advantages of miniaturization and affordability, NIR spectroscopy has overtaken the other vibrational spectroscopic techniques as a handheld device. The present communication will thus focus primarily on the building principles of commercially available handheld NIR spectrometers and discuss their potential use with respect to selected in-the-field and on-site applications for material testing and authentication.

2. Instrumentation

In Fig. 2 a selection of commercially available handheld NIR spectrometers based on different monochromator/detector principles are shown alongside information on their available wavelength ranges, spectral resolution and signal/noise ratio (only instruments for which reliable information on these parameters was available, are included). Some of these instruments have been tested for specific quantitative and qualitative applications and for the comparison and ranking of their performance the reader is referred to the relevant literature (10-12). The good results achieved in feasibility studies have launched the idea of making handheld NIR spectrometers in the near future available to a non-expert user community for private use in everyday life, e.g., quality control and detection of counterfeits in pharmaceuticals, food and materials (13,14).

Generally, recent progress in NIR spectrometer miniaturization has taken advantage of new micro-technologies, such as MEMS (Micro-Electro-Mechanical Systems) and MOEMS (Micro-Opto-Electro-Mechanical Systems) (15,16). Based on the type of detector, handheld NIR spectrometers can be classified into two categories: array-detector and single-detector instruments. Probably the first commercial, real light-weight, handheld (<100 g) NIR spectrometer (VIAMI Solutions Inc. (formerly JDSU) MicroNIR 1700, Santa Rosa, CA, USA) has an array detector that covers the wavelength range from 908 - 1676 nm and uses a linear variable filter (LVF) as monochromator (Fig. 2a). It has so far been used for many applications ranging from the

authentication of seafood and determination of food nutrients to the analysis of hydrocarbon contaminants in soil and authentication and quantitative determination of pharmaceutical drugs (11,13, 17-19). However, in the NIR wavelength range where Indium-Gallium-Arsenide (InGaAs) is the preferred detector material, the price for a single detector is much lower compared to an array detector. Therefore, in an attempt to further reduce the hardware costs, new developments focus on systems with single detectors. Thus, the DLP NIR scan Nano EVM, for example, is based on Texas Instruments's (USA) digital micro-mirror device (DMD™) in combination with a grating and a single-element detector, and also covers the wavelength range from 900 - 1701 nm (Fig. 2b). Recently, a MEMS-based FT-NIR instrument, containing a single-chip Michelson interferometer with a monolithic opto-electro-mechanical structure, has been introduced by Si-Ware Systems (Egypt). Contrary to most other handheld spectrometers, this FT-NIR instrument can scan spectra over the large wavelength range from 1298 - 2606 nm (Fig. 2d). Other MEMS-based FT-NIR systems have been put on the market by Southnest Technology (China) and Hamamatsu Photonics (Japan)(Figs. 2e/f). Spectral Engines (Finland) developed miniaturized NIR spectrometers, that are based on a Fabry-Perot etalon (Fig. 2c), which acts as a tunable wavelength filter. In order to cover the NIR wavelength region 1350 - 2450 nm, however, four spectrometers are required. Handheld NIR instruments based on grating micro-spectrometers are offered by InSION GmbH (Germany) and OtO Photonics (Taiwan)(Figs. 2 h/i). A new kind of handheld NIR scanner – the SenoCorder Solid - with unique detectors made of organic solar cells has been recently introduced onto the market by Senorics GmbH (Germany)(Fig. 2g). In this device, each of the 16 detectors with active areas of 6.25 mm² absorbs only a limited wavelength range within 400 – 1800 nm, and therefore no monochromator is required. For the work presented in this communication, a scanner operating in the wavelength range 1170 - 1675 nm has been utilized.

3. Applications

In what follows, selected application examples from food/material authentication and geological exploration using different handheld systems will be outlined in some detail, in order to demonstrate the experimental effort and data evaluation procedure before a qualitative or quantitative calibration model can be used in industrial or everyday life routine.

3.1 Identification of peony seed oil

The beautiful peony flower has not only a high ornamental value, but also a high nutrition and health care function. In Fig. 3 a simple pictorial representation of the production steps for peony seed oil is shown. The final product is a pure natural yellow edible oil, in which the total content of unsaturated fatty acids, including α -linolenic acid (ω -3 fatty acid), linoleic acid, and oleic acid, is > 90.0%(w/w). The ratio of ω -3/ ω -6 fatty acids is about 1: 4, which equals the proportion of ideal human intake. In addition, it contains abundant healthy active substances such as squalene, flavonoids, and polyphenol compounds [20-22]. Because of its value for the human body, it enjoys great popularity. However, the final production output of peony seed oil is low, which leads to a high market price of about 90 US\$/500ml. In order to avoid fraud by fake products, a rapid authentication procedure by handheld NIR spectroscopy was tested in a feasibility study and is described in some detail in this section. In this qualitative application example, the MicroNIR 1700 instrument (Fig. 2(a)) combined



with a liquid-sample accessory (Fig. 4) was applied for the recording of spectra for the development of a calibration model for the rapid discrimination of peony seed oil from other oil species. 18 Peony seed oil and 19 other oil samples, collected from different oil factories, were used as calibration set to build a principal component analysis (PCA) model. For external validation of the identification/discrimination performance of this PCA calibration model, a test set consisting of 9 peony seed oils and 10 other oil samples was collected (Tab.1).

For the transfection measurements, a drop of oil was deposited in the trough of the liquid-sample accessory, and then the lid was closed (Fig. 4A/B). Fifty scans with an integration time of 60 ms were accumulated for the wavelength range 950 - 1650 nm with a spectral resolution of 12.5 nm. A 99% Spectralon™ reflection standard (Labsphere Inc., North Sutton, USA) was used as reference. The final spectrum was the average of triplicate measurements.

Tab. 1 Composition of the calibration and test set for the development of a PCA calibration model.

Oil	# Samples	
	Calibration	Test
Olive	1	1
Sunflower	7	4
Blended	5	2
Corn	5	3
Sesame	1	0
Peony	<u>18</u>	<u>9</u>
Total	37	19

NIR spectra frequently contain background information, drift, and noise, and in order to obtain reliable, accurate, and stable calibration models, it may be necessary to preprocess the spectral data before modeling [23]. In this application, the spectra were pretreated by the standard normal variate (SNV) scatter correction. For data evaluation, different chemometric analyses were applied. The PCA model was developed with the spectra of the calibration samples and its identification performance was verified with the spectra of the test set samples; additionally, a soft independent modeling of class analogies (SIMCA) model was used to test the identification capability for the spectra of the test set. The spectral pretreatment, PCA, and SIMCA algorithms were performed using the Unscrambler™ software (version 10.X, CAMO Software AS, Oslo, Norway).

In Fig. 5A, the raw spectra of the calibration samples are shown. The most intense peak at 8343 cm^{-1} and the shoulder at 8660 cm^{-1} are the 2nd overtones of the $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ vibrations, respectively. The absorption bands at 7243 cm^{-1} and 7114 cm^{-1} can be assigned to the $2\nu(\text{CH}_3)+\delta(\text{CH}_3)$ and $2\nu(\text{CH}_2)+\delta(\text{CH}_2)$ combination bands [24], respectively, superimposed by the 1st overtone of the $\nu(\text{OH})$ stretching vibration. After SNV pretreatment, especially the spectral differences in the $8000 - 9000\text{ cm}^{-1}$ wavenumber range were highlighted (Fig. 5B).

PCA is a statistical algorithm that uses an orthogonal transformation to change a set of related variables into a set of linearly uncorrelated variables (principal components, PCs). After the



application of PCA to a spectral data set, the number of PCs is lower than the original variables. This reduction of PCs allows patterns in the data set to be easily visualized and analyzed. In PCA, variables that are strongly correlated in the original data set remain closely related in the new components, and data points that are similar in the original data set also cluster in the PC space [25,26]. In Fig. 6A the 3D-PCA score plot based on the first three PCs is shown for the calibration samples (red and blue circles). The peony seed oil was clearly discriminated from the other oil species and the test samples were assigned to the correct clusters (blue and red triangles).

The SIMCA method has been widely applied in NIR spectroscopy for a broad range of applications, such as the identification of pharmaceutical excipients, detection of parasites in cod fillets, authentication of fish, textiles and polymers [10, 27-29]. It is a classification method analyzing similarities, and it is based on separate PCA models (disjointed modeling) of the investigated classes (in the present case two classes of oils). The SIMCA classification uses the PCA models developed for the spectra of different classes to assess to which class an unknown sample belongs. The classification result is represented in a so-called Coomans plot, and in the present case, the peony seed oil identity can be achieved if the spectra of the unknown test samples were assigned to the relevant quadrant defined by the SIMCA model. In Fig. 6B the Coomans plot (5% significance) represents the unambiguous discrimination of peony and non-peony oil samples by assigning the spectra of the test set correctly to the corresponding quadrants. Thus, it has been proved by this feasibility study, that handheld NIR spectroscopy can be utilized for the discrimination of peony oil from other oil samples.

3.2 Detection of cotton in silk/cotton textiles

Due to its extraordinary tribological properties silk is an extremely popular material for customer applications such as clothes, quilts, furniture and carpets. As pointed out in a well-known Chinese trade internet portal, the quilts are often adulterated with cotton, polyester, or other, lower-quality materials, which can lead to large price fluctuations. This situation is frequently misused in popular tourist centers or online portals to sell a blended fabric as pure silk for unrealistic prices to credulous customers. Additionally, silk is often blended with cotton to weave fabrics with different appearances and body feelings. However, the rapid identification of the silk (or non-silk) content in clothes, quilts, or carpets is difficult for ordinary customers.

NIR spectroscopy has proved a suitable tool for identifying textile materials not only with laboratory benchtop instruments [30], but also with handheld NIR spectrometers [27]. However, no quantitative NIR analysis of cotton/silk blends for the rapid detection of adulteration or quality control has so far been reported in the literature. In the present feasibility study, the MEMS-based handheld FT-NIR spectrometer (Si-Ware Systems) (Fig. 2d) and the Seno Corder Solid scanner (Senorics GmbH) (Fig. 2g) were used for this purpose and tested for their performance to rapidly determine the cotton content in silk textiles.

For the development of a quantitative partial least squares (PLS) calibration model, pure silk threads were purchased from Zhejiang Hangzhou satin company (Hangzhou, Zhejiang, China), and pure cotton threads were supplied by Hebei Sanli Wool Textile Co., Ltd (Baoding, Hebei, China). Each thread was cut into a very short length of about 0.5 mm so that the final material looked like a powder. Then, different weights of silk and cotton were mixed, and 101 blend samples were prepared,

in which the cotton content varied from 0 to 100% (w/w) with concentration intervals of 1.00% (w/w). Of this sample set, 20 samples with cotton content between 3.00% and 98.00% (w/w) were selected in intervals of 5.00% (w/w) as the test set, and the residual 81 samples were used as the calibration set to develop the PLS models. The test set samples were used as external samples to validate the performance of the PLS models.

The statistics of the reference values of the total sample set, and the calibration and test sets, respectively, are summarized in Tab. 2. The similarity of the mean, maximum, and minimum values and the range, standard deviation, and variances demonstrated that the data sets provided a reasonable basis for evaluating the calibration performance of the different instruments.

Tab. 2 Statistics of the cotton content values (% (w/w)) of the different sample sets.

Data sets	Mean	Max	Min	Range	Std.	Variance
Total	49.99	100.00	0.00	100.00	29.30	858.50
Calibration	49.88	100.00	0.00	100.00	29.37	862.70
Test	50.51	98.07	3.08	94.99	29.54	872.77

For the sample presentation of the MEMS-based handheld FT-NIR spectrometer (Si-Ware Systems), each sample was arranged as an approximately 3mm layer on top of the sapphire window of the instrument and covered by a 99% Spectralon™ reflection standard (Labsphere Inc., North Sutton, USA) (Fig. 7a). The diffuse reflection spectra were recorded bottom-up in the wavelength range 1347-2543 nm (7423–3932 cm^{-1}), with 10 s measurement time, Happ-Genzel apodization, and 32 K FFT points. Taking into account the heterogeneity of the investigated samples, triplicates (repacks) of each sample were measured and stored via Bluetooth on a Samsung Tablet and finally averaged before further processing. In Fig. 7b, exemplarily the spectra of pure silk (red) and pure cotton (blue) are shown for this instrument. For the measurement with the SenoCorder Solid (Senorics GmbH), samples were also positioned on the window of the instrument (Fig. 7c), and covered with the reflection reference mounted in the instrument's lid. Triplicate measurements were conducted in the wavelength range from 1170-1675 nm (8547–5970 cm^{-1}) with 16 variables and with a spectral resolution of 67 nm (averaged). Spectra of pure silk (red) and pure cotton (blue) measured with this instrument are shown in Fig. 7d.

The primary chemical structures of cotton (cellulose) and silk (fibroin protein) are significantly different. Thus, specifically the instrument with the long-wavelength (short-wavenumber) extension (Si-Ware Scanner) reflected significant differences of the pure cotton and pure silk spectra in the 5500 – 4000 cm^{-1} range of the $\nu(\text{OH})+\delta(\text{OH})$, $\nu(\text{NH})+\delta(\text{NH})$, $\nu(\text{NH})+\text{Amide I}$, $\nu(\text{NH})+\text{Amide II}$, $\nu(\text{CH}_2)+\delta(\text{CH}_2)$ and $\nu(\text{CH}_3)+\delta(\text{CH}_3)$ combination bands (Fig. 7b). Some variations - although less characteristic - can also be observed in the 7500 – 6000 cm^{-1} wavenumber range, where the absorption bands of the first overtones $2\nu(\text{OH})$ and $2\nu(\text{NH})$ and the combination vibrations $2\nu(\text{CH}_2)+\delta(\text{CH}_2)$ and $2\nu(\text{CH}_3)+\delta(\text{CH}_3)$ are located. Similarly, minor changes between the pure cotton and silk spectra were detected in the 6000 – 5000 cm^{-1} region of the $2\nu(\text{CH})$, $2\nu(\text{CH}_2)$ and



2xv(CH₃) overtones. Due to its narrow wavenumber/wavelength range, and the small number of available data points for the total spectrum, very small qualitative differences between pure cotton and silk are observable in the spectra measured with the SenoCorder Solid (Fig. 7d) spectrometer.

Spectral preprocessing can significantly improve the calibration model performance because NIR spectra frequently contain background information, drift, and noise. Thus, in order to obtain reliable, accurate, and stable calibration models, it is recommended to preprocess spectral data before modeling (23). In the present investigation, the extended multiplicative scatter correction (EMSC) and 1st derivative, respectively, were applied for the raw spectra measured with the FT-NIR (Si-Ware Systems) spectrometer and the SenoCorder Solid (Senorics GmbH) as optimal pretreatment method. In the Figs. 8a-d the raw calibration spectra and their pretreated analogs are presented for the two instruments. Especially the pretreated spectra demonstrate a significantly larger response to changes of the cotton/silk-ratio for the MEMS FT-NIR system compared to the SenoCorder Solid (Fig. 8c/d).

After data pretreatment, PLS calibration models were developed for the cotton content of the blend samples with the 81 spectra of the calibration set using the Unscrambler™ software (version 10.X, CAMO Software AS, Oslo, Norway). Internal cross-validation (CV) was applied to select the optimal number of factors (31). This validation procedure estimated the prediction error by splitting all samples into 20 segments, of which one segment was retained for validation, and the remaining 19 segments were used for calibration. This process was repeated until all segments were used for validation once (32). Finally, the 20 test set samples were used to demonstrate the predictive capability for the cotton content of “unknown” samples. The calibration statistics output includes the root mean square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV), root mean square error of prediction (RMSEP), and the R² of the calibration, cross-validation, and prediction sets, respectively (Tab. 3). The residual predictive deviation for cross-validation (RPD_{cv}) was calculated as the ratio of the standard deviation of the reference data to RMSECV (33,34). Investigations by William and Sobering (34) suggest that an RPD >2.5 is acceptable, whereas a value >5.0 reflects sufficient accuracy for quality control.

Tab. 3 Comparison of the calibration and prediction performance for the cotton content in silk/cotton blends based on the NIR spectra of the two handheld instruments

Instruments	Pretreatment	Number of Factors	R ²			RMSE (%(w/w))			RPD _{cv}
			Cal.	CV.	Test	Cal.	CV.	Test	
			Si-Ware Scanner	EMSC	2	0.9895	0.9891	0.9904	
SenoCorder Solid	1 st derivative	5	0.9858	0.9826	0.9787	3.48	3.92	4.12	7.49



While the R^2 parameters are very close for both instruments, the RMSE values of approximately 3%(w/w) and 4%(w/w) clearly prove a much higher prediction performance for the Si-Ware instrument. Apart from the RMSE and R^2 values, another parameter that has a significant effect on the performance of the developed calibration model is the number of factors (31). Fewer factors lead to lower accuracy, because less information is applied. On the other hand, too many factors frequently induce over fitting with only an apparent improvement of predictive ability for the calibration set, because the calibration model will have a lower prediction performance when applied to unknown samples. In the present work, the optimal number of factors was chosen when the RMSECV changed least with a further increase of the number of factors and when the difference between RMSEC and RMSECV was the lowest. The number of factors for the PLS calibrations derived with the spectra of the two different instruments are also included in Tab. 3. Only two factors were required for the PLS calibration developed with the spectra of the MEMS FT-NIR (Si-Ware Systems) spectrometer, whereas five factors were necessary for the calibration with the spectra measured with the SenoCorder Solid (Senorics GmbH) instrument. This difference is mainly a consequence of the available wavelength/wavenumber ranges, which provided more or less information on chemical functionalities. For the RPDs, the ranking is clearly Si-Ware scanner > SenoCorder Solid instrument, although the value for the last mentioned instrument clearly testifies fitness for use in routine quality control.

3.3 Quantitative analysis of aluminum in geological test samples for bauxite exploration

Bauxite is an aluminum ore consisting mainly of the aluminum minerals gibbsite (hydrargillite) $\gamma\text{-Al(OH)}_3$, boehmite $\gamma\text{-AlO(OH)}$, diaspor $\alpha\text{-AlO(OH)}$, furthermore the iron oxides hematite Fe_2O_3 and goethite FeO(OH) , the clay mineral kaolinite and small amounts of the titanium oxide anatase TiO_2 . It owes its name to its first locality Les Baux-de-Provence in southern France, where it was discovered in 1821. From the annual global supply rate of approximately 370 million tons the largest mining activities are located in Australia, Guinea, China, Brazil, Indonesia and India. Thus, frequently exploration work is conducted in remote places, where a fast evaluation of geological test samples regarding the content of the relevant minerals is of utmost importance. In this respect handheld NIR spectrometers could in the near future play an important role, because they can be used on-site to quickly analyze milled geological rock samples with reference to a rapid go/no-go decision regarding a possible exploration of the investigated site.

Based on previous expertise in the successful quantification of hydrocarbon content in soils with different handheld NIR spectrometers (18,29), we were asked to provide a scientific basis for the practical application of handheld NIR spectroscopy in bauxite exploration. The aim of this project was to test the applicability of a portable, handheld NIR spectrometer for real-time and on-site measurements to discover viable deposits. For the planned feasibility study Alcoa Corp. (Australia) supplied 90 ground rock samples with known content of aluminum (0 - 54% (w/w)) for calibration and 10 anonymous test samples (after prediction disclosed with 0 - 47% (w/w) Al-content) for external validation. Diffuse-reflection spectra were recorded with a handheld NIR spectrometer based on a LVF monochromator (MicroNIR 1700, VIAVI Solutions Inc., USA), and a PLS calibration model for Al-content was developed. Finally, the performance of this calibration model was evaluated by the comparison of the predicted and reference values of the test samples.



The scientific foundation, why a NIR spectrometer can be utilized instead of a handheld XRF instrument to predict the Al-content in milled rock samples, is provided in Fig. 9. The two NIR spectra in the large box have been recorded with a benchtop instrument of samples with Al-contents of 0.0 %(w/w)(blue) and 53.6%(w/w)(red), whereas the insert shows the spectra of the same samples measured with the handheld spectrometer used for the feasibility study. Thus, the red spectrum of the sample with the high Al-content reflects a multiplicity of absorption bands in the wavenumber range 6000-7500 cm^{-1} , that belong to 2xv(OH) overtones in different hydrogen bonding states of the Al-minerals described above. The spectrum of the sample without aluminum, on the other hand, shows only a few bands in this spectral range, that originate from 2xv(OH) overtones of silicate minerals. Although the handheld NIR spectrometer has a limited wavelength/wavenumber range and a much lower spectral resolution, the spectroscopic footprint of the OH-overtones, that correlates with the Al-content, is clearly available. Based on this correlation, the PLS calibration for the Al-content has been developed with the available calibration spectra. The spectra were recorded with the VIAVI Micro NIR 1700 LVF spectrometer in the wavelength range 908-1676 nm (11013 – 5966 cm^{-1}) at a spectral resolution of 12.5 nm and a scan time of 2.5 seconds (integration time/scans: 50ms/50) utilizing an uncooled InGaAs (128 pixels) detector. For sample presentation a small brass cup was customized (Fig.10), and due to the dark coloration of the samples the 50% Spectralon™ reflection standard (Labsphere Inc., North Sutton, USA) was used as reference. To compensate sample heterogeneity, triplicates (repacks) of each sample were measured with subsequent averaging of the spectra before further processing. In Fig. 11 a/b the raw spectra and the 2nd derivative spectra of the calibration set are shown. As final pre-processing only the wavenumber range 8000 – 6150 cm^{-1} was retained after truncation of non-relevant spectral regions. The PLS calibration model for the Al-content was developed with the Unscrambler™ Software (v.10.3) (Camo AS, Norway) and the actual/predicted plot is shown with the calibration and cross-validation parameters in Fig. 12. Based on two principal components only, and RMSE values of 4.35 %(w/w) and 4.49 %(w/w) for the calibration and cross-validation, respectively, a useful calibration model and instrumental tool has been provided for a rapid assessment of the investigated site. In Tab. 4 the prediction of unknown test samples (T1-T10), which were not contained in the calibration set, clearly supports the application of handheld NIR spectroscopy for bauxite exploration studies. It is of note, that samples, which did not contain aluminum, were frequently predicted with negative values.

Tab. 4 External validation by comparison of actual versus predicted values of 10 test samples.

Test Sample	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Actual %(w/w)	0.0	5.1	10.3	15.5	20.2	25.0	30.3	35.6	40.4	43.0
Predicted %(w/w)	-4.2	13.9	15.6	15.1	18.0	24.9	34.9	39.1	41.0	35.7

4. Conclusions

Generally, hand-held instruments have launched vibrational spectroscopy into a new era of real-time, in-the-field and on-site analysis. Of the different types of instrumentation, however, miniaturization of NIR spectrometers has reached a superior level compared to Raman and MIR spectrometers.



Furthermore, high-volume manufacturability has considerably reduced the costs for handheld NIR spectrometers, and will contribute towards a broader dissemination of such instruments for everyday-life applications. Notwithstanding this optimistic prospects, the objective of this communication is to turn readers' attention to the realistic potential of state-of-the-art handheld NIR spectrometers for qualitative and quantitative quality control. For this purpose, concrete examples have been presented, because we are firmly convinced that in the near future these miniature handheld spectrometers will not only enable industrial and academic spectroscopists, but also a non-expert user community in new measurement environments to gain significant benefits. Thus, we can foresee, that such miniaturized spectrometers - especially if they are integrated into mobile phones and equipped with user-friendly evaluation software - gain widespread public adoption beyond first responders, police and customs forces, and food inspection agents or military personnel. Attempts of deception with fake pharmaceuticals, silk carpets blended with cotton or polyester and bastard amber, could be consigned to the past, together with the issues we now have with food quality, adulteration, and authentication. Despite these positive prospects, we would like to end with some words of caution: if the interest of readers in handheld NIR spectrometers has been sparked, they should make sure to critically scrutinize the technical background of new, elaborately advertised products - particularly "scanners" offering food and life-science applications with instant cloud evaluation - because many of these instruments appear to lack realistic feasibility.

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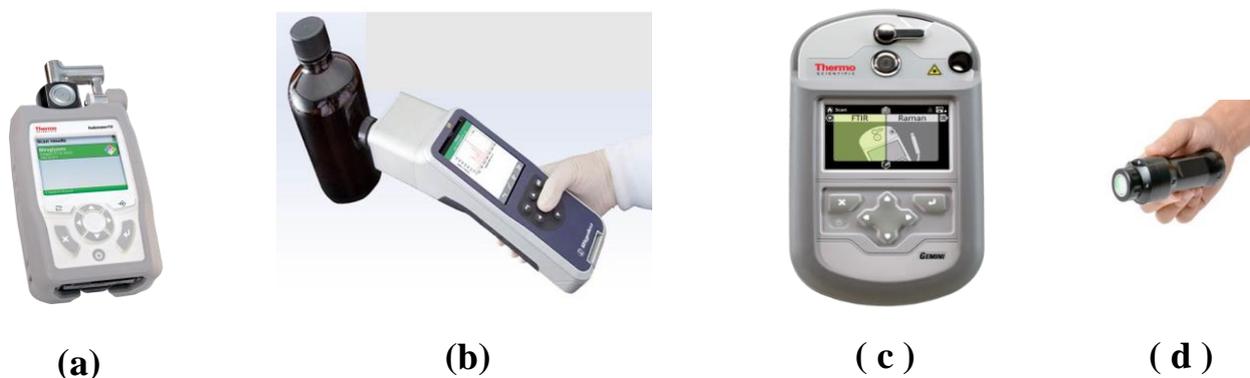
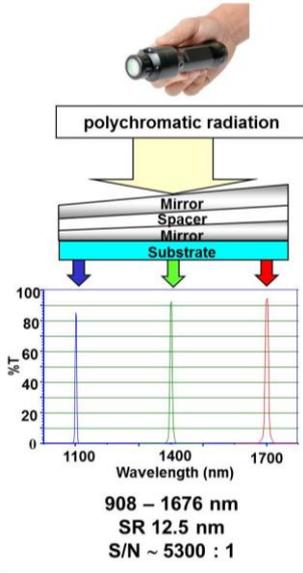
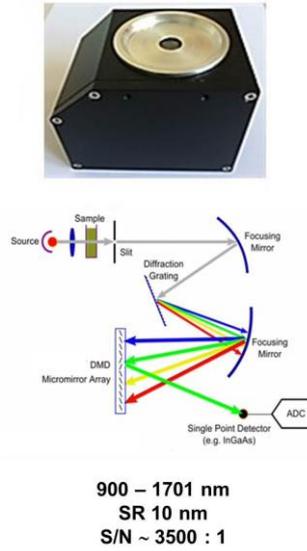


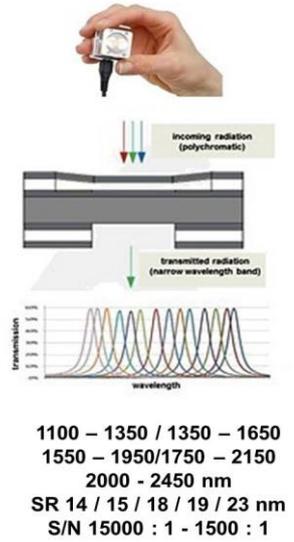
Fig. 1 Examples of handheld vibrational spectrometers: (a) TruDefender™ FT-IR spectrometer (Thermo Fisher Scientific, USA); (b) Progeny, Raman spectrometer (Applied Rigaku Technologies, Inc., USA); (c) Gemini Analyzer, combined Raman/FT-IR spectrometer (Thermo Fisher Scientific, USA); (d) MicroNIR 1700 (VIAVI Solutions Inc., USA).



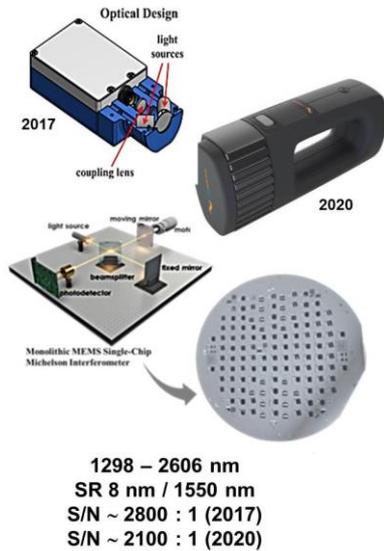
(a)



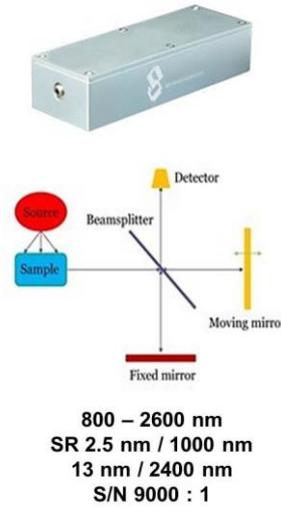
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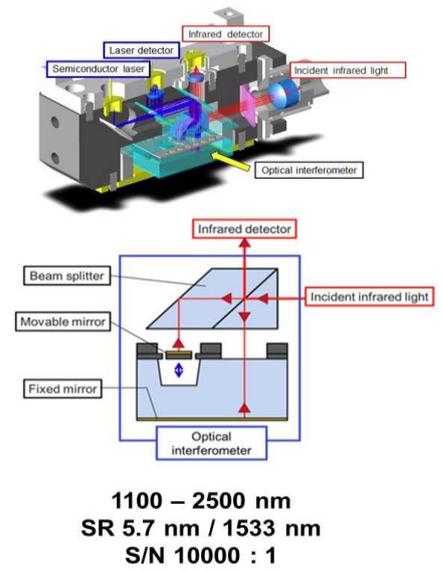
(c)



(d)



(e)



(f)

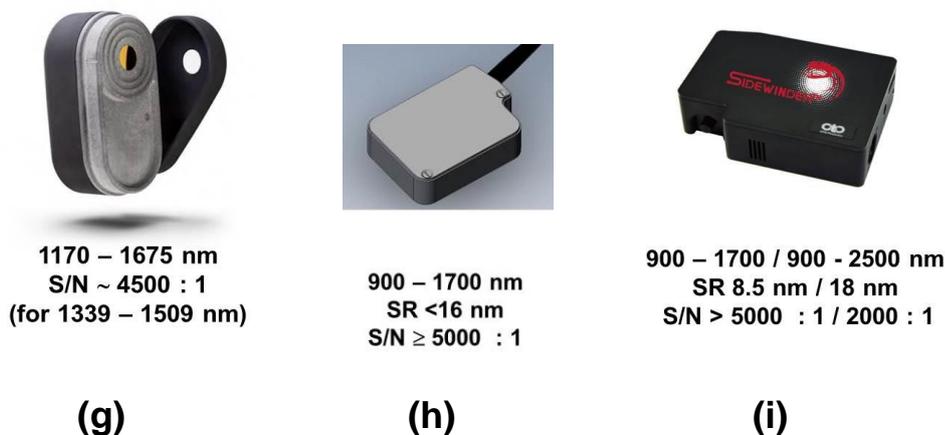


Fig. 2 Handheld NIR spectrometers with different monochromator/detector principles: (a) MicroNIR 1700, linear variable filter (VIAVI Solutions Inc., USA); (b) NIRscan Nano EVM, Digital Mirror Device (DMD™)(Texas Instruments, USA); (c) NIROne, Fabry Perot Tunable Filter (Spectral Engines, Finland); (d) MEMS FT-NIR (Si-Ware Systems, Egypt); (e) MEMS FT-NIR (Southnest Technology, China); (f) MEMS FT-NIR (Hamamatsu Photonics, Japan); (g) SenoCorder Solid with 16 solar cell detectors (Senorics GmbH, Germany); (h) NIR Grating Microspectrometer (Insion, Germany); (i) NIR Grating Spectrometer (OtO Photonics, Taiwan).



Fig. 3 Pictorial representation of production steps for Peony seed oil.

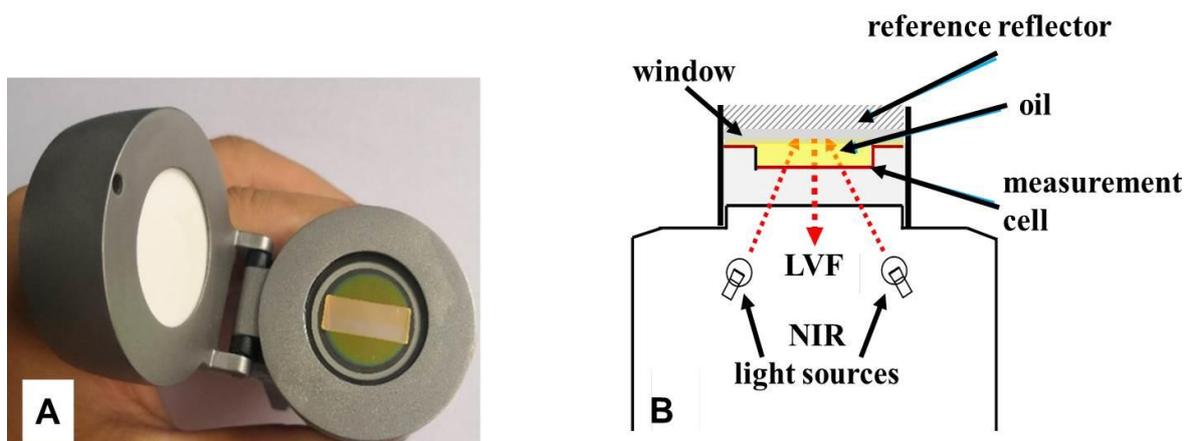


Fig. 4. MicroNIR 1700 handheld spectrometer with a liquid-sample accessory for measuring oil samples (A), and schematic diagram of the liquid-sample accessory (B).

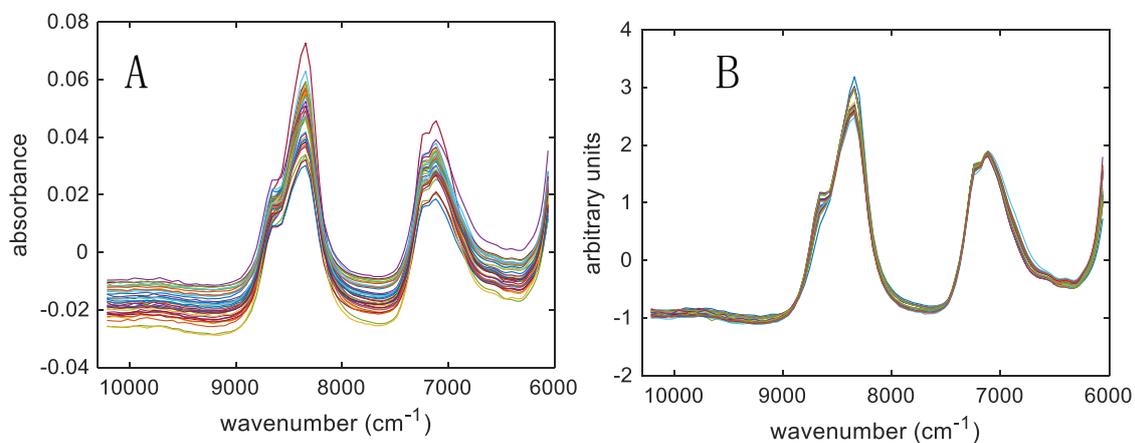


Fig. 5 Raw spectra and SNV pretreated spectra of the peony seed oil calibration samples.

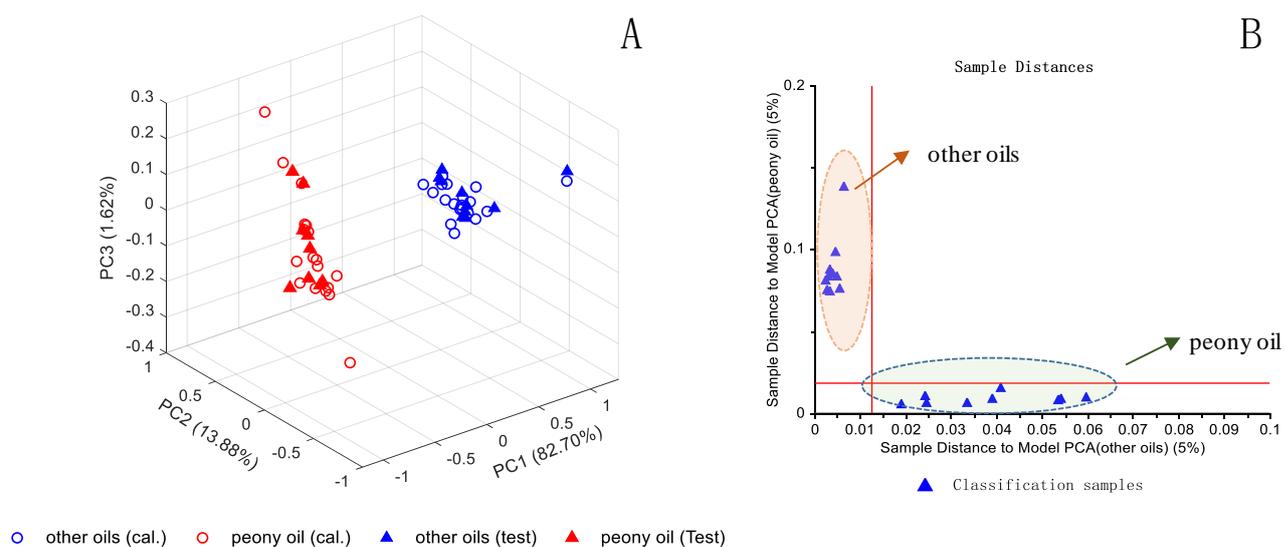


Fig. 6 Three-dimensional PCA score plot for the calibration and test set samples of peony seed oil and other oil species (A) and Coomans plot for the spectra of test samples of peony seed oil and other oil species (B).

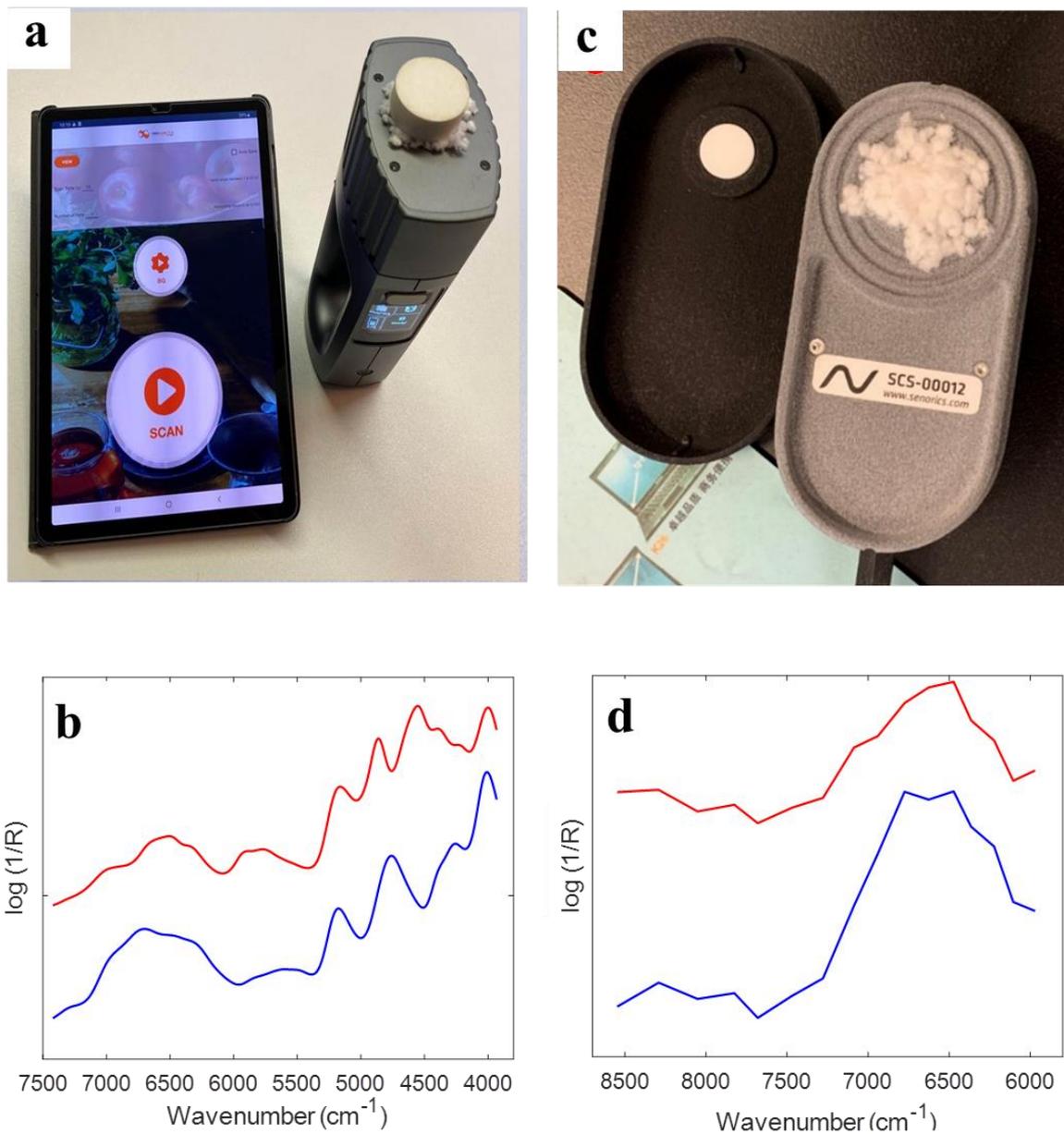


Fig. 7 Sample presentation and spectra of pure cotton (blue) and silk (red) for the Si-Ware Scanner (a/b) and SenoCorder Solid (c/d).

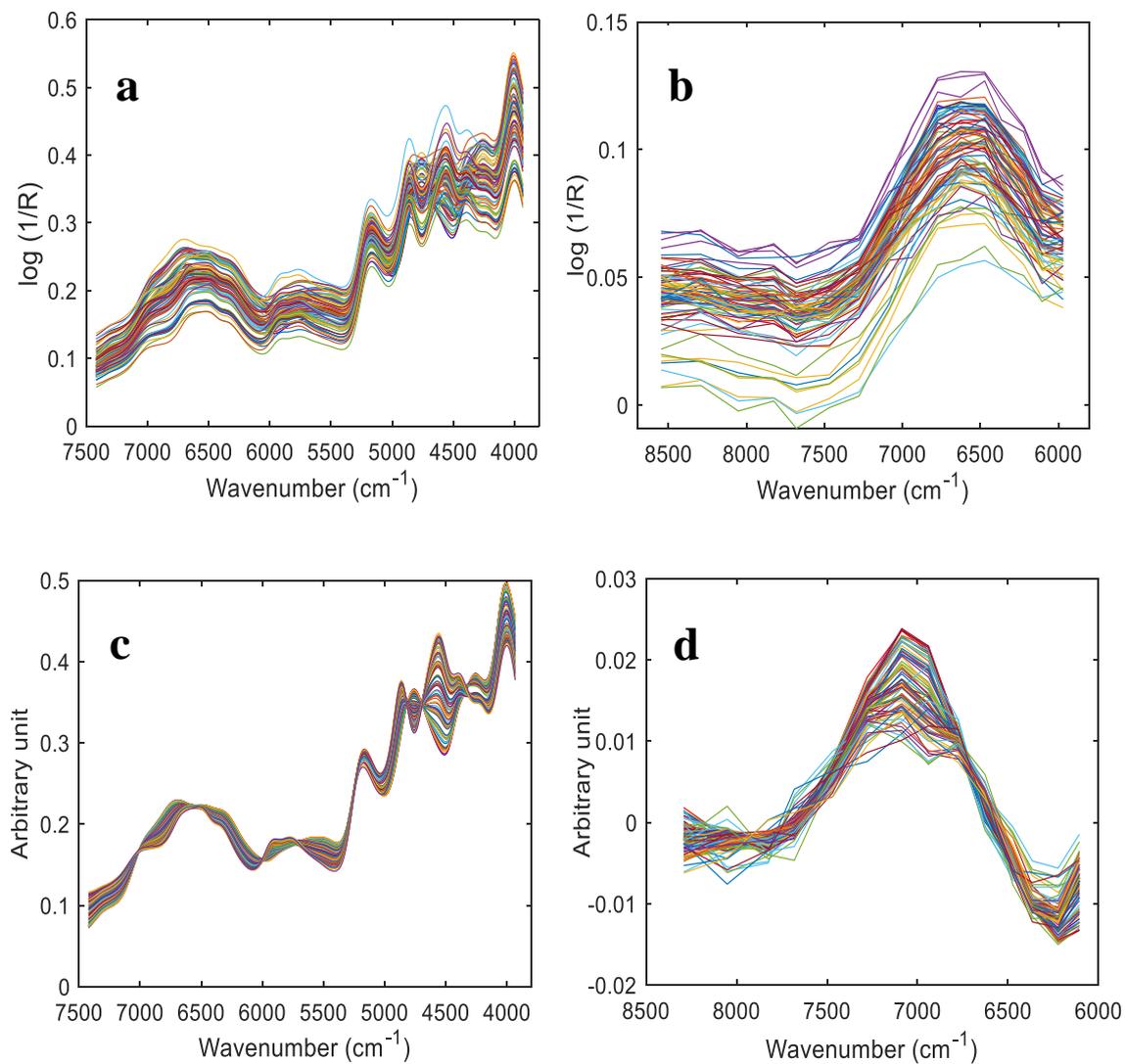


Fig. 8 Raw calibration spectra measured with the Si-Ware MEMS FT-NIR (a) and the SenoCorder Solid (b) spectrometers and their EMSC (c) and 1st derivative (d) pretreated analogs.

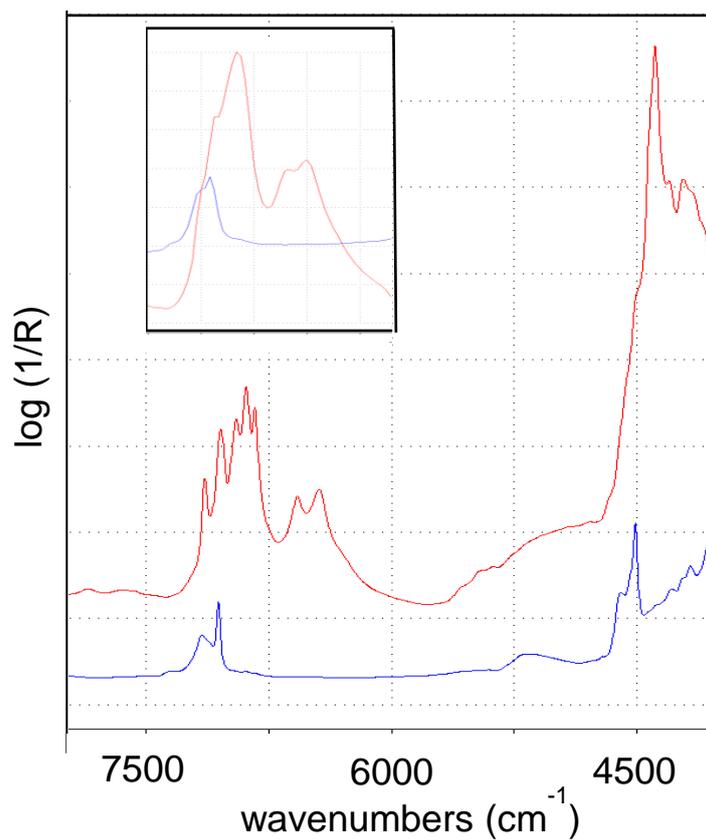


Fig. 9 NIR spectra of two samples with different Al-content (blue: 0.0% (w/w); red: 53.6% (w/w)) measured with a benchtop FT-NIR spectrometer (VECTOR 22N, Bruker Optik GmbH, Germany). The insert shows the NIR spectra of the same samples measured with a handheld NIR spectrometer (MicroNIR 1700, VIAVI Solutions Inc., USA).

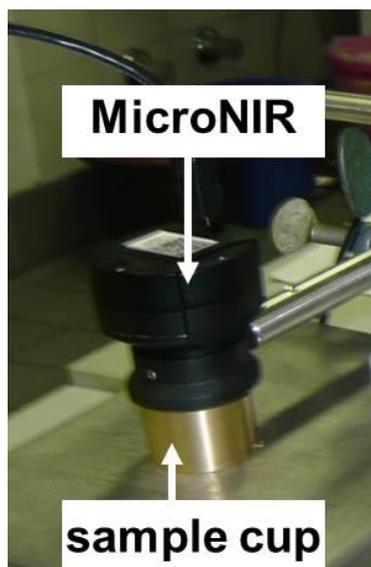
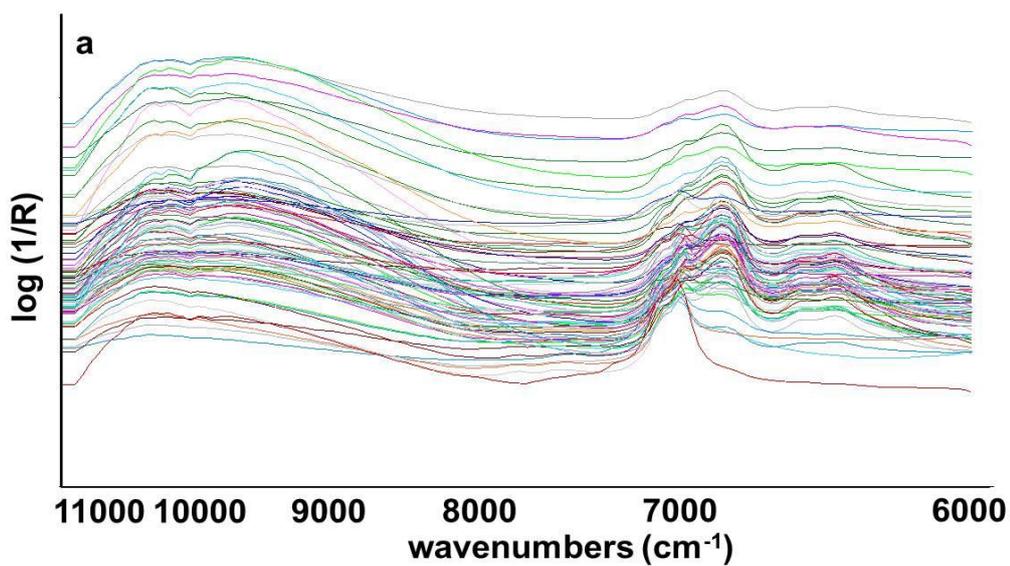


Fig. 10 Experimental set-up for the recording of NIR diffuse reflection spectra of the milled rock samples (presented in a customized brass cup) with the handheld MicroNIR 1700 spectrometer.



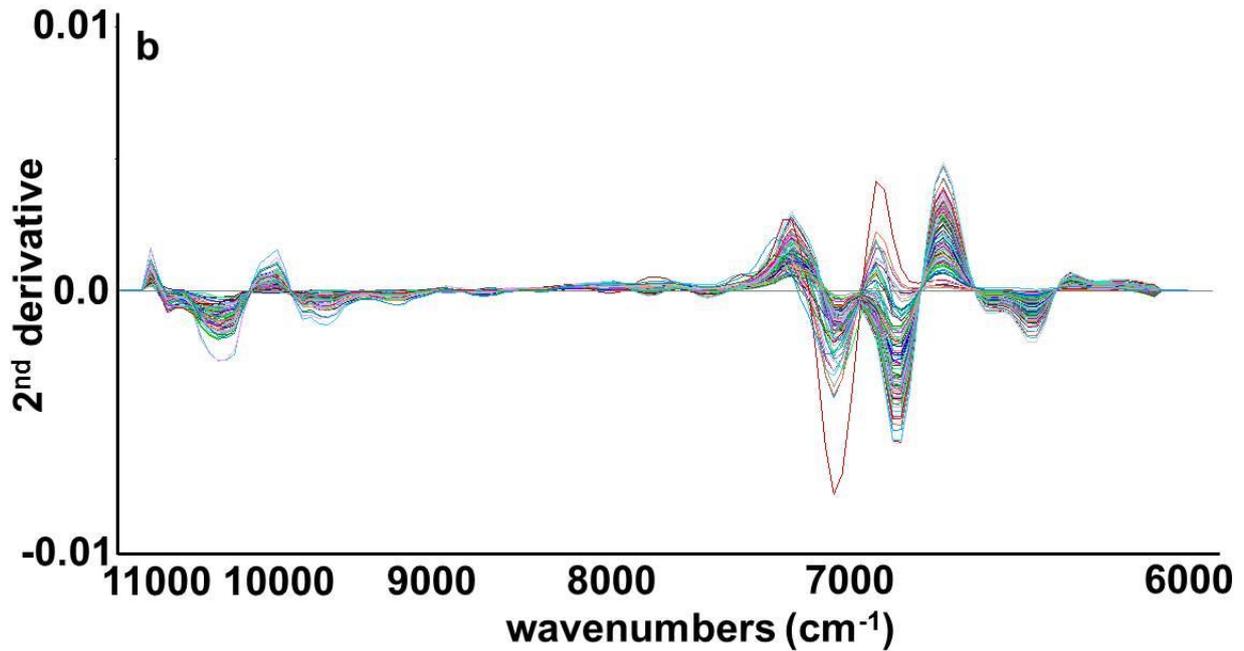


Fig. 11 Original NIR spectra of the calibration samples (a) and same spectra after 2nd derivative pretreatment for the development of a PLS calibration model of Al-content in the milled rock samples (b).

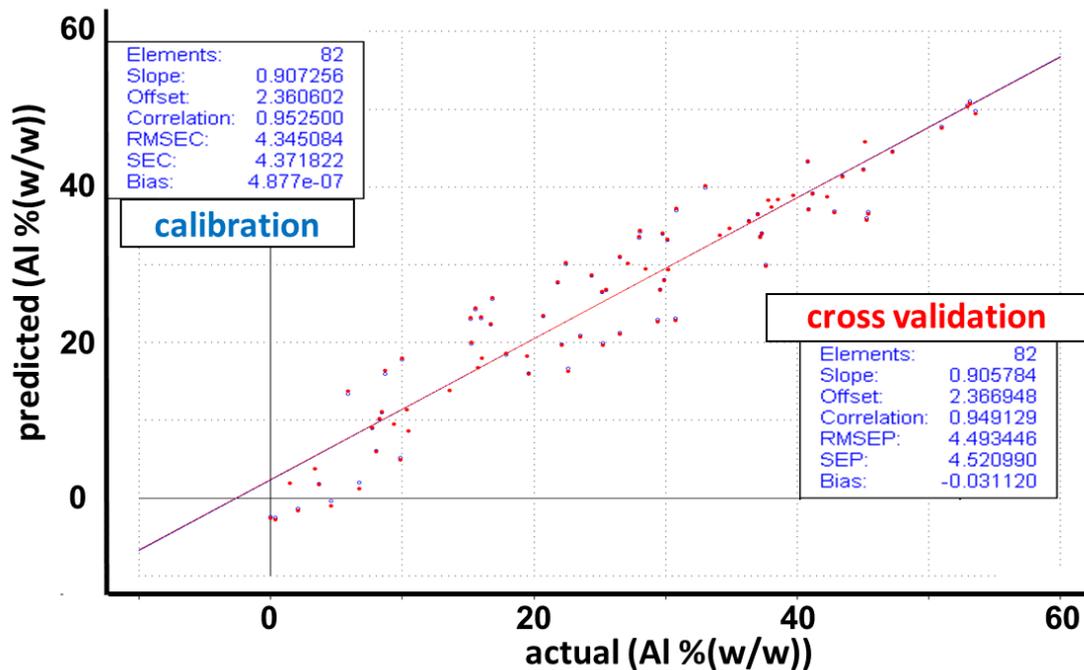


Fig. 12 Actual/Predicted plot of the PLS calibration for Al-content in milled rock samples with calibration and cross-validation parameters, based on 82 calibration spectra (after removal of 8 outliers) and 2 factors.