

Miniature Near-Infrared (NIR) Spectrometer Engine For Handheld Applications

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Miniature Near-Infrared (NIR) Spectrometer Engine For Handheld Applications

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ABSTRACT

While substantial progress has been made recently towards the miniaturization of Raman, mid-infrared (IR), and near-infrared (NIR) spectrometers, there remains continued interest from end-users and product developers in pushing the technology envelope toward even smaller and lower cost analyzers. The potential of these instruments to revolutionize on-site and on-line applications can only be realized if the reduction in size does not compromise performance of the spectrometer beyond the practical need of a given application. In this paper, the working principle of a novel, extremely miniaturized NIR spectrometer will be presented. The ultra-compact spectrometer relies on thin-film linear variable filter (LVF) technology for the light dispersing element. We will also report on an environmental study whereby the contamination of soil by oil is determined quantitatively in the range of 0-12% by weight of oil contamination. The achieved analytical results will be discussed in terms of the instrument's competitiveness and suitability for on-site and in-the-field measurements.

Keywords: miniaturized near-infrared spectrometer, linear variable filter (LVF), hydrocarbon contamination, soil contamination, handheld spectrometer, NIR spectrometer.

1. INTRODUCTION

Miniaturization of vibrational spectrometers began approximately a decade ago, but only within the last few years have real handheld Raman, infrared (IR), and near-infrared (NIR) scanning spectrometers become commercially available. These new developments were partly driven by the potential and advantages of microelectromechanical systems (MEMS) production, and in the near future will prove their impact for in-the-field and on-site analysis. To date, primarily qualitative applications^{1,2} have been demonstrated for homeland security, threat detection, and forensic investigations, whereas only a few quantitative studies have been reported³⁻⁶. Only recently an extensive review of handheld vibrational spectrometers and their performance tests for multi-component analysis of solid and liquid samples has been published⁷.

Apart from discussing the instrument details of JDSU's MicroNIR spectrometer (MicroNIR), the objective of this communication is to report the test results obtained with this miniaturized spectrometer system for the quantitative determination of oil contamination in soil.

The contamination of soil with hydrocarbons (oil, gasoline, diesel) due to accidents or leakages is a wide-spread phenomenon with potential health risks. At present no technique is available for fast on-site identification and determination of the identity and amount of contamination. This information is necessary to determine remediation methods for decontamination of the area under consideration (excavation, biotechnical method). All methods currently practiced, require the isolation of the contamination with a subsequent quantitative spectroscopic or chromatographic determination⁸.

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Halogenated hydrocarbons were previously in use as extraction solvents, but due to their toxicity and ozone-depleting properties, they have been replaced by halogen-free solvents. Microwave-assisted extraction has since been proposed as a time-saving alternative⁹. In all cases, however, soil samples have to be retrieved and transported to the laboratory for qualitative and quantitative analysis, which is a time-consuming process. The approach of diffuse reflection measurements with a handheld NIR spectrometer completely replaces classical methods with the future aim of a qualitative and quantitative in-situ analysis. To reach this aim the mobility of a handheld instrument has to be combined with on-site evaluation of spectroscopic data by chemometric calibration techniques. Thus, large-area investigations would allow a fast assessment of the measures to be taken in the case of a hazardous incident. Furthermore such on-site measurements would allow a very effective monitoring of the success of decontamination measures. The method is not limited to the characterization of areal pollution only, but can also be easily extended to depth-profiling assessments.

2. METHODOLOGY

2.1 Instrumentation

The MicroNIR is a new instrument designed to measure diffuse reflectance in the NIR region of the electromagnetic spectrum. The MicroNIR owes its small size to the novel thin-film linearly variable filter (LVF) used as the dispersive element. The LVF is a dielectric thin-film Fabry-Perot bandpass filter deposited using energetic processes, well-known to produce stable and reliable optical components¹⁰. The filter coating in the LVF is intentionally wedged in one direction. Since the center wavelength of the bandpass filter is a function of the coating thickness, the peak transmitted wavelength varies continuously along the direction of the wedge. This working principle is illustrated in Figure 1. The LVF component can be compared to a scanning Fabry-Perot interferometer that scans with position instead of time.

The MicroNIR employs an LVF component directly bonded to a linear detector array, which results in an extremely compact and rugged spectral engine with no moving parts. The LVF makes each pixel of the detector respond to a different wavelength. This ultra-compact spectroscopic engine is coupled with miniaturized readout electronics and a tungsten lamp diffuse illumination system. The entire unit is USB-powered and scarcely larger than a golf ball. An image of the MicroNIR spectrometer is provided in Figure 2.

Figure 3 shows a schematic illustration of MicroNIR's optical design. In the diffuse reflection mode, shown in Figure 3a, two built-in tungsten lamps flood-illuminate a spot on the sample under test that is approximately 3mm in diameter, at a 3mm distance from the instrument. The diffuse reflected radiation is collected and delivered to the spectral engine, which is read by the electronics and displayed on a computer. Although optimal working distance is approximately 3mm, longer working distances are also possible, which can be useful for transflection applications (viewing a white standard through a sample liquid, for example). Figure 3b shows the MicroNIR in a transmission configuration. An external lamp illuminates a cuvette with collimated light, and the MicroNIR is used with lamps off to measure the transmission.

Key attributes of the MicroNIR spectrometer are summarized in Table 1. The MicroNIR used for the study in this paper was tailored to monitor the wavelength range of an extended indium gallium arsenide (InGaAs) detector, covering 1150-2150nm (8695-4651cm⁻¹ in wavenumber range). The standard InGaAs detector wavelength range is another common option of MicroNIR covering 950-1650nm (10,526-6060cm⁻¹). Other custom wavelength ranges are possible. The MicroNIR used for this study had a 128-pixel detector array, recording data every 8nm with a spectral resolution of about 1.25% of center wavelength. In other words, at a wavelength of 2000nm, the spectral resolution is 25nm. Other spectral resolution levels can be attained through changing the number of pixels in the detector array or changing bandwidth of the LVF bandpass.

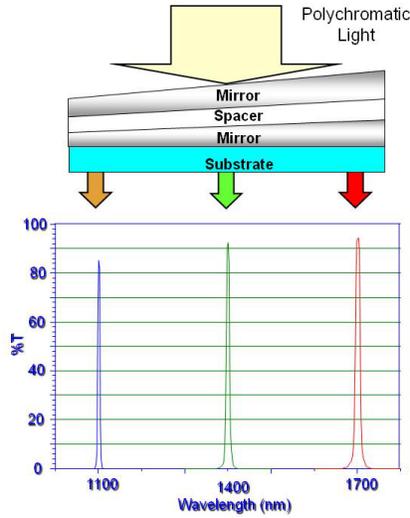


Figure 1: Working principle of a linear variable filter (NIR) component. The wedge in the thickness is applied to all layers comprising the bandpass filter design.



Figure 2: The MicroNIR spectrometer.

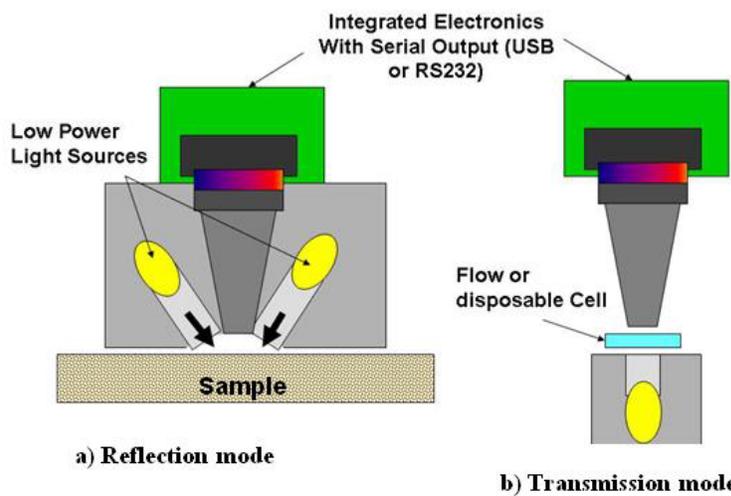


Figure 3: An illustration of the optical design of MicroNIR in a) diffuse reflection mode, and b) transmission mode.

Table 1: Key performance attributes of the MicroNIR spectrometer.

Weight	60 grams
Dimensions	45mm diameter x 42mm height
Spectral Range	Extended: 1150-2150nm; Standard: 950-1650nm
Optical Resolution	<1.25% of center wavelength, i.e. at 1000nm wavelength, resolution is <12.5nm; at 2000nm, <25nm resolution.
Geometric Resolution	Extended: 8nm per pixel; Standard: 6.25nm per pixel
Power Requirement	USB powered, <500mA at 5V
Operating Temperature	-20°C to 40°C

2.2 Materials

For the sample preparation, a standard soil type 2.1 (silty sand, which was purchased from LUFA (Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Germany) was used. The most important property parameters of this soil type are summarized in Table 2. To prepare soil samples homogeneously contaminated in the concentration range from 0 – 12 % (w/w), the corresponding amount of motor oil (Aral, Tronic 15W-40 SAE) was dissolved in methylenechloride (CH₂Cl₂) and 43 g of soil was saturated with this solution. Then, the methylenechloride was completely evaporated in a drying oven for 1 hour at 60°C and finally the soil sample was measured in a Petri dish at 5 different positions (Figure 4) at room temperature (22-24°C). In total, 48 oil-contaminated soil samples (43 calibration and 5 test samples) were prepared and measured according to this procedure. In Table 3 the composition of the calibration (Table 3a) and test samples (Table 3b) is summarized. For the MicroNIR scans, the reference measurements were performed with a 10% Spectralon™ reflectance standard before and after each soil sample measurement. The integration time of MicroNIR was set to 1000 microseconds. The total number of samples taken per scan was set at 10,000, hence a total of 10seconds of scan time per soil sample was used. As stated in section 2.1, the wavelength range of MicroNIR used in this study was 1150-2150 nm (8695-4651 cm⁻¹).

Table 2: Selected property parameters of the standard soil type 2.1

Standard Soil Type	2.1 Silty Sand
Sampling Date	March 22, 2011
Org. C in %	0.68 ± 0.15
Nitrogen in %N	0.04 ± 0.01
Particles < 0.02 mm in %	7.7 ± 2.4
pH-Value (0.01 M CaCl ₂)	5.1 ± 0.4
Cation Exchange Capacity (meq/100 g)	4.0 ± 1.0

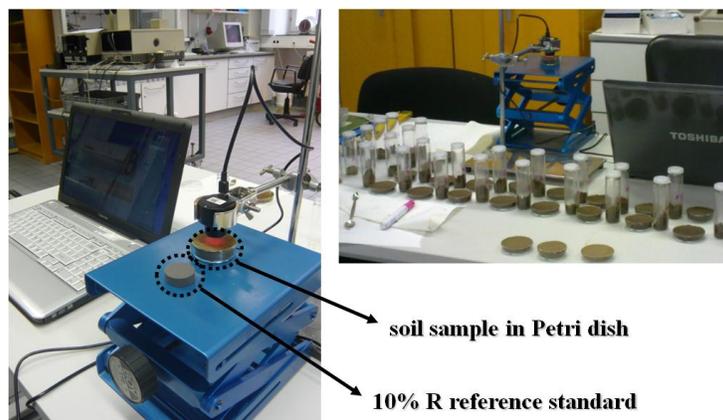


Figure 4: Soil sample measurement with MicroNIR spectrometer.

Table 3a: Composition of the oil-contaminated soil samples of the calibration set.

Calibration Sample	Concentration (%w/w)	Calibration Sample	Concentration (% w/w)	Calibration Sample	Concentration (% w/w)
1	0.00	16	4.25	31	8.25
2	0.25	17	4.50	32	8.75
3	0.50	18	4.75	33	9.00
4	1.00	19	5.00	34	9.25
5	1.25	20	5.25	35	9.50
6	1.50	21	5.50	36	9.75
7	1.75	22	5.75	37	10.00
8	2.00	23	6.25	38	10.25
9	2.25	24	6.50	39	10.75
10	2.75	25	6.75	40	11.00
11	3.00	26	7.00	41	11.25
12	3.25	27	7.25	42	11.50
13	3.50	28	7.50	43	12.00
14	3.75	29	7.75		
15	4.00	30	8.00		

Table 3b: Composition of the oil-contaminated soil samples of the test set.

Test Sample	Concentration (% w/w)
Test 1	0.75
Test 2	2.50
Test 3	6.00
Test 4	8.50
Test 5	10.50

2.3 Chemometric Data Evaluations

The pretreatment of data, development of the cross-validated PLS-1 calibration model for the oil contamination and the prediction of the independent test samples were performed with The Unscrambler™ software (version 9.6; CAMO Software AS, Oslo, Norway).

3. RESULTS AND DISCUSSION

Five replicate spectra were recorded from each of the 48 oil-contaminated samples and subsequently the mean of the replication spectra and a Savitzky-Golay smoothing (9 data points, 3rd degree polynomial) was calculated. In Figure 5, the mean spectra of the 43 calibration samples are shown in the wavenumber range 7670-4953 cm⁻¹ (1304-2019 nm). For the development of the PLS-1 calibration model, only the 2 x ν(CH) overtone region 6139-5294cm⁻¹ (1629-1889 nm) was used (Figure 5b). The calibration/cross validation parameters for the PLS-1 calibration model are summarized in Figure 6. Based on 2 factors and 2 outliers only, very good calibration and cross-validation parameters have been obtained. The predictions of the mean spectra of the 5 test samples with this calibration are represented in Table 4 and demonstrate the good agreement with the reference values over the whole concentration range.

4. CONCLUSIONS

Despite the heterogeneity of the soil samples, excellent results have been obtained with the MicroNIR spectrometer for the quantitative determination of oil contamination in soil samples, thus showing promise for on-site, real-time evaluation of contaminated soil for remediation applications. The MicroNIR spectrometer is expected to find use in numerous other applications that benefit from in-the-field measurement and for real-time investigation, for both qualitative and quantitative assessments.

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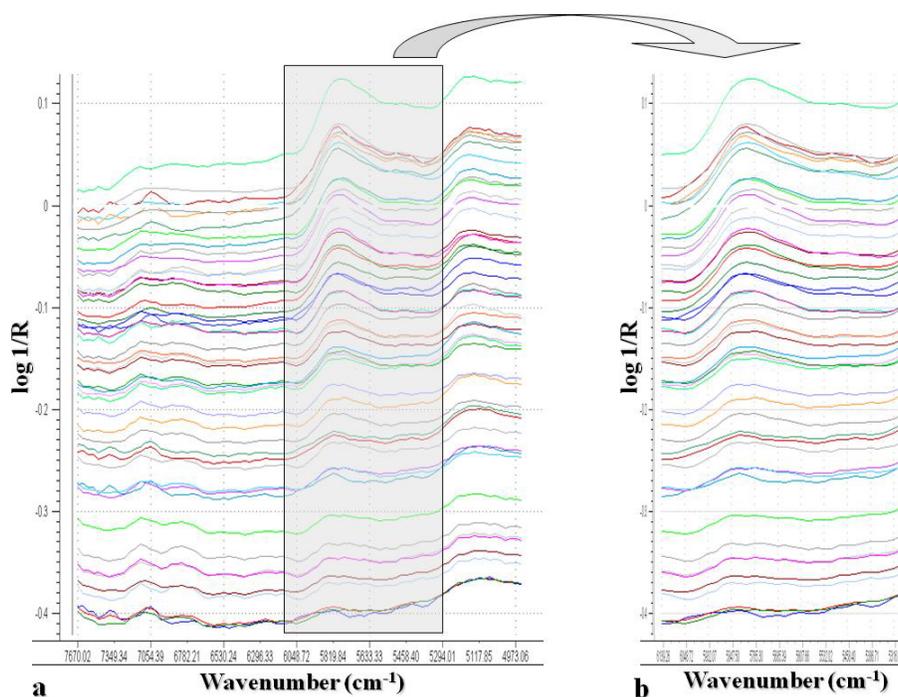


Figure 5: NIR spectra (mean of 5 replicates) after Savitzky-Golay smoothing, (a): 7670-4953 cm^{-1} , and after wavenumber selection for calibration, (b): 6139-5294 cm^{-1} .

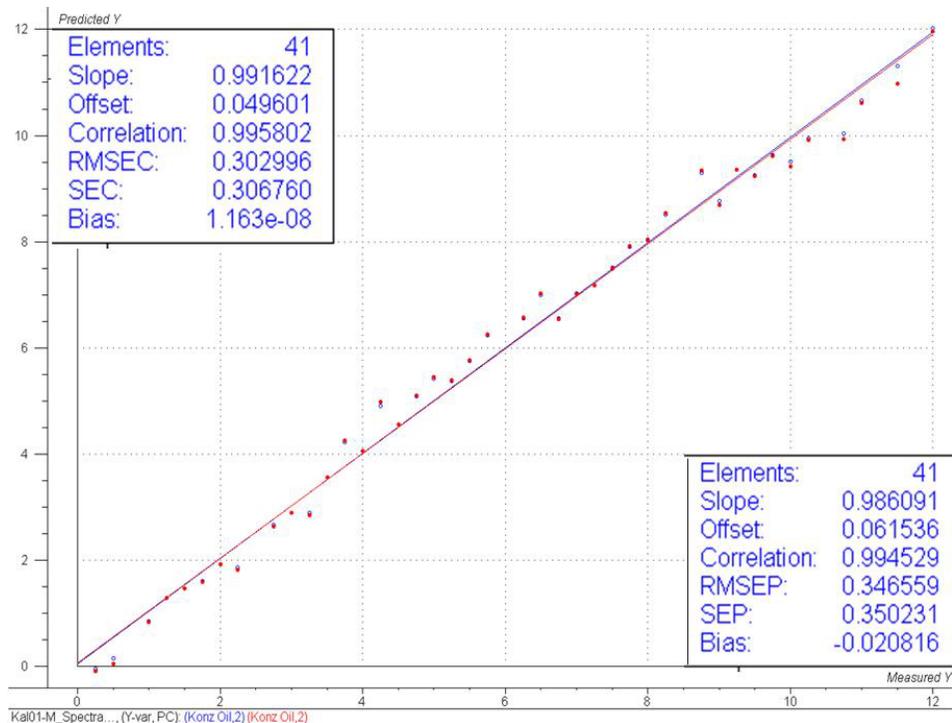


Figure 6: PLS 1 calibration/cross-validation parameters for oil contamination in soil.

Table 4: Prediction of the oil content of contaminated test-set samples.

Test Sample	Reference (% w/w)	Prediction (% w/w)
Test 1	0.75	0.95
Test 2	2.50	2.70
Test 3	6.00	6.19
Test 4	8.50	8.22
Test 5	10.50	10.29

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