Short communication

Low-cost handheld NIR spectroscopy for identification of organic solvents and low-level quantification of water contamination

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ABSTRACT

Quality control of liquid raw materials arriving on an industrial manufacturing site is typically performed in a dedicated laboratory using time- and chemicals-consuming analytical methods. Herein, we report the successful development of a handheld near-infrared spectroscopy method for the rapid, low-cost testing of organic solvents. Our methodology enables the classification of organic solvents with 100% accuracy and the quantification of water in methyl ethyl ketone with a precision of ~0.01 wt% in the 0–0.25 wt% range. The accessory that we have developed for the NIR sensor enables the development of a broad range of sensing applications on organic liquid systems.

1. Introduction

Organic solvents are indispensable for a large variety of industrial chemical operations. With an estimated annual production volume of 20 million metric tons [1], they are essential for chemical reactions, separation processes, product handling and cleaning. In view of the often toxic nature of non-renewable, fossil fuel-derived solvents and their detrimental impact on the environment, major efforts are ongoing to reduce usage of these solvents and develop more sustainable alternatives based on, for example, ionic liquids, deep eutectic solvents, and supercritical fluids [2].

On industrial production sites it is common practice to verify the identity of solvents delivered to the site and to assess their purity. This happens before the solvent is transferred to storage tanks, because of the potentially major safety and economic consequences when different solvents are inadvertently mixed on a multi-m^3 scale. Verification is commonly done in a quality control (QC) laboratory using physical measurements such as (a combination of) density and refractive index, or more chemically specific infrared (IR), near-infrared (NIR) or Raman spectroscopy methods, whereas specific water contamination is often quantified by Karl Fischer titration. For example, the feasibility of

benchtop, laboratory-based NIR instruments for the development and transferability of a spectral library for the identification of common organic solvents has been demonstrated before [3]. Analysis speed and cost would be further reduced substantially if such laboratory-based methods could be replaced by low-cost, handheld sensors that enable operators to perform the required analyses close to their relevant location.

Rapid progress is being made in the development of handheld spectroscopy devices and their applications in a variety of industries [4, 5]. The handheld device (SCiO) used in the research presented here has recently seen a variety of qualitative and quantitative applications, such as identification of counterfeit drugs [6], crop cultivars [7], dried bloodstains [8], analysis of total antioxidant capacity of gluten-free grains [9], and determination of water and fat content in cheese [10].
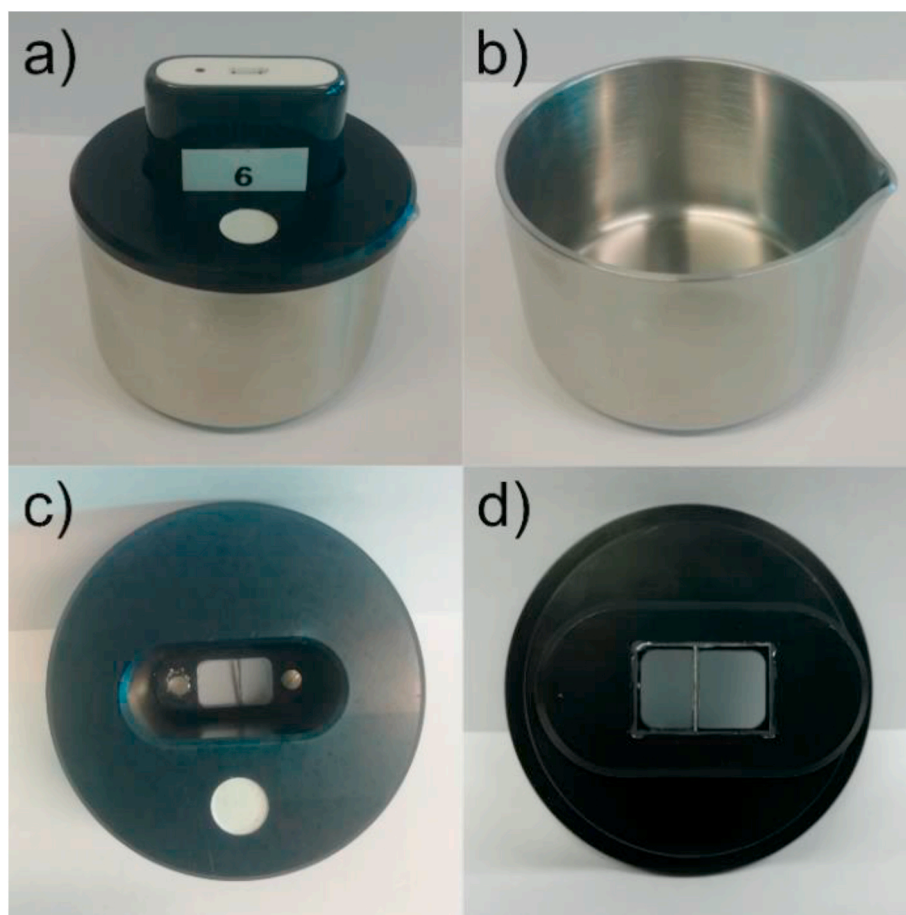
Here we present a novel application: the development of a low-cost NIR method for the perfect identification of nine organic solvents. Next to that, research is presented towards quantification of water contamination in industrially relevant levels.

Fig. 1. In-house developed accessory (patent pending) made from black-anodized aluminum for using the SCiO NIR sensor with organic solvents. (a) Front view with a SCiO sensor inserted into the holder and the holder positioned over a stainless-steel beaker (b). Empty stainless-steel beaker. (c) Top view. The glass and magnets of the original SCiO accessory were glued in the holder with Scotch Weld 2216 epoxy adhesive. (d) Bottom view showing the glass windows.

2. Experimental

2.1. Materials

As handheld spectroscopic device the SCiO NIR sensor v1.2 (sold by Consumer Physics since 2016) was used. This device has an array of 12 separate photodiode detectors, each with a separate optical filter. This results in measurements in the short-wave part of the NIR spectrum (740–1070 nm, see also [11] for more properties and limitations of the device) and is predominantly used in diffuse reflection mode on solid samples. Reported applications for liquids are scarce so far [12]. An important reason for this is that the accessory that Consumer Physics offers for measurements in liquids is not suitable for organic solvents. We therefore developed our own accessory that can be positioned on the rim of a stainless-steel beaker (Fig. 1). This allowed us to perform transflection measurements on solvents with an optical path length of 20 mm using the bottom of the beaker as reflecting surface. For all studies, near infrared spectra were collected by filling the beaker with enough solvent (with or without water contamination) such that the lower part of the holder was submerged. Experience has shown that the battery level of the device affects the total signal that is obtained from a scan (lower battery means lower total signal). The device was therefore continuously kept at full charge by connecting it to a power bank.
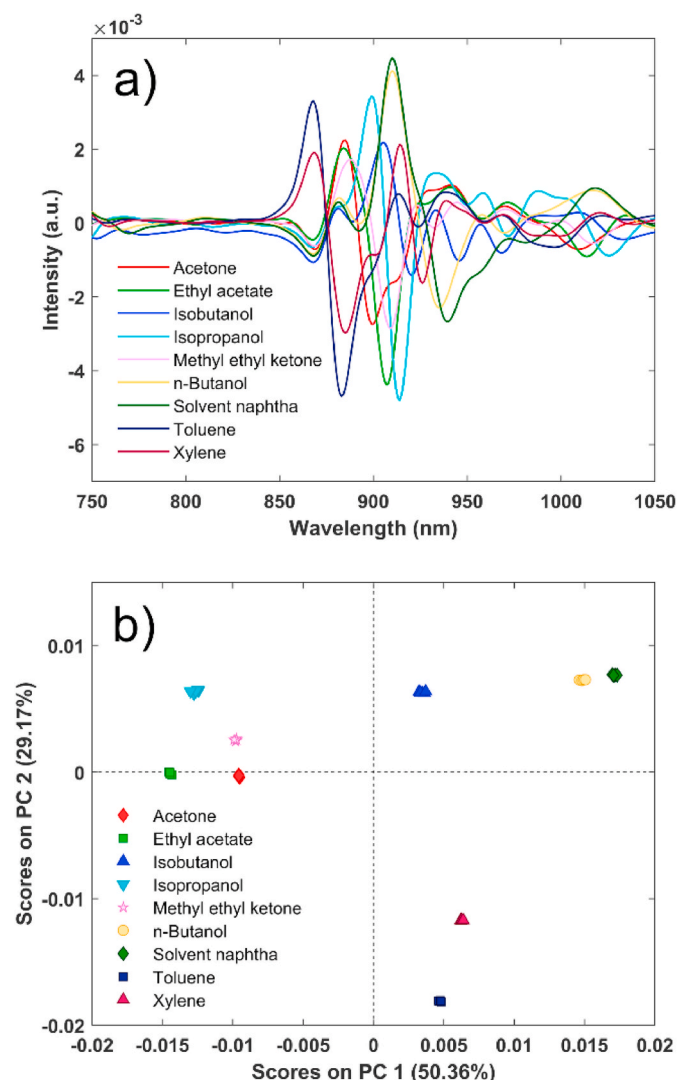
Depending on the specific application, water concentration in a solvent may have an upper specification limit in the ppm to percentage range. Water displays strong bands in many regions of the NIR spectral range, which is utilized for a variety of qualitative and quantitative applications in the emerging field of aquaphotomics [13]. In the short-wave NIR region, the second overtone of the O–H stretching band $(3\nu_{1,3})$ of water absorbs at around 970–980 nm. Because the SCiO sensor operates in the 740–1070 nm range, we investigated its feasibility to quantify water in selected solvents.

To test the performance of the SCiO sensor at industrially relevant water contamination levels (0–0.25 wt%), we spiked a different solvent methyl ethyl ketone (MEK) with known amounts of water and recorded short-wave NIR spectra of these samples in triplicate and repeated this procedure on a second day, always using the same SCiO scanner. The calibration set obtained in this way was used to develop a Partial Least Squares (PLS) regression model for water concentration. Similar measurements on newly prepared samples (independent from the calibration set) were then used to validate the water concentration PLS model.

As conventional benchmark for the performance of the SCiO NIR sensor, we repeated the full experiment by measuring the same water-spiked MEK samples in glass vials (inner diameter 6.8 mm = optical path length) on a benchtop FT-NIR instrument (Bruker Tango) in transmission mode. We used the spectral region (1860–1930 nm) containing the strong NIR combination band $(\nu_{1,3} + \nu_2)$ of water at 1907 nm. This band is blue-shifted compared to the corresponding band at 1940 nm in bulk water due to the large differences in intermolecular H-bonding between bulk and MEK-diluted water [14]. The data from the benchtop device were analyzed with PLS regression after the data was preprocessed with Savitzky-Golay 1st derivative followed by mean centering.

Since the spectral region from the handheld and benchtop are not the same, a final PLS regression model was made from data collected with the benchtop device, but only using data from the spectral region that is
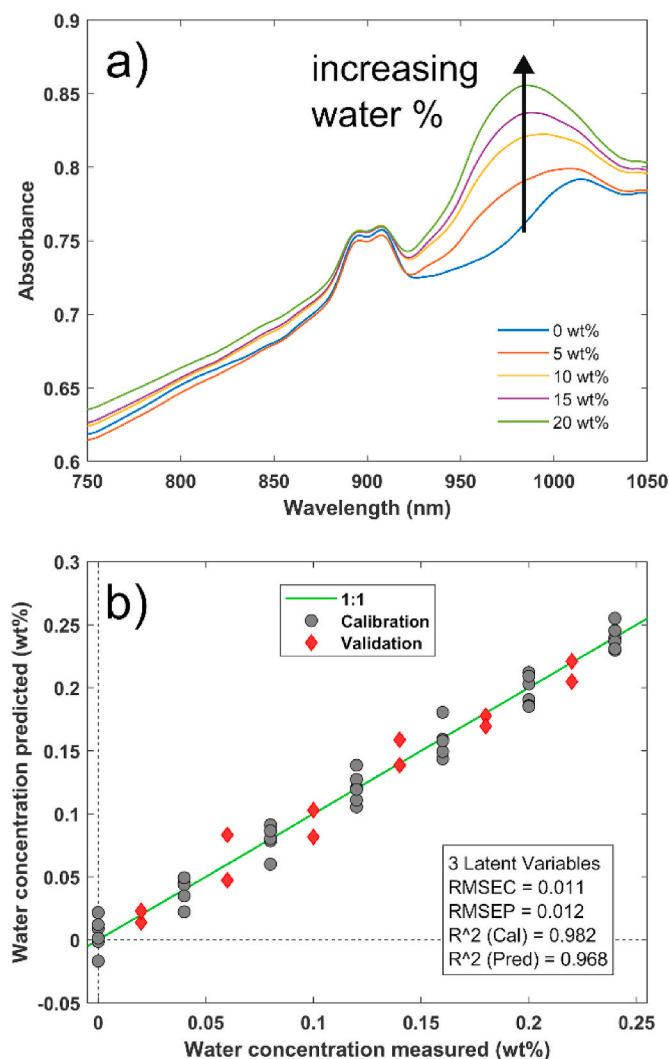
Fig. 2. Preprocessed SCiO NIR spectra of 9 different organic solvents. Spectra were preprocessed by converting transmission to absorbance values, followed by Savitzky-Golay 1st derivative (2nd order, 15-point window) and mean centering. (b) PC 2 vs. PC 1 score plot from PCA applied to the preprocessed spectra shown in (a). Each solvent was measured with 5 different SCiO scanners, as can be seen by the occurrence of 5 identical symbols for each solvent in the score plot.

shared by both devices (i.e., 870–1070 nm).

3. Results and discussion

Fig. 2a shows preprocessed SCiO spectra of multiple measurements of the nine solvents. Strong features are observed mainly between 840 nm (11,900 cm^{-1}) and 1040 nm (9615 cm^{-1}), which can be assigned predominantly to third overtones of aliphatic and aromatic C–H stretch vibrations and the second overtone of the O–H stretch vibration [15]. The distinct spectral differences observed between these solvents suggest that solvent classification in the short-wave NIR range is feasible with the SCiO sensor. This hypothesis was confirmed by Principal Component Analysis (PCA) of the preprocessed spectra, which shows well-separated clusters for the solvents in the PC 2 vs. PC 1 score plot (Fig. 2b). Each solvent was measured with five different SCiO sensors, Fig. 2b shows that the variation between sensors is much smaller than the variation between solvents. Further analysis (not shown) of this data using clustering (hierarchical cluster analysis) and classification (partial least squares discriminant analysis, Random Forest) techniques resulted

Fig. 3. (a) Raw absorbance NIR spectra of acetone spiked with different concentrations of water. (b) Predicted vs. measured plot for water concentration in MEK from PLS regression (wavelength range 740–1070 nm, preprocessing: Savitzky-Golay 1st derivative followed by mean centering). For the calibration set, each sample was measured in triplicate on 2 different days, producing 6 measurements for each concentration level. For the prediction set, each sample was measured once on 2 different days.

in 100% correct solvent classification for the calibration data as well as for a test set measured independently. We therefore concluded that the SCiO sensor can distinguish the selected organic solvents with perfect accuracy, which is a promising result for potential deployment in industrial settings. The data acquired in this study are available online [16].

For the quantification of water in solvents, Fig. 3a shows how high concentrations of water in acetone are readily observed by the $3\nu_{1,3}$ band with a peak maximum at 980 nm. Fig. 3b shows the average precision (expressed as Root Mean Square Error of Prediction) of 0.012 wt %, when quantifying the water concentration in the MEK samples spiked with water, measured with the SCiO scanner. The regression vector of the PLS model shows the water band as main feature (Fig. S1), confirming the model's selectivity towards the NIR water band. Like the solvent identification results, this result is of considerable promise for industrial application. For direct comparison: the PLS regression using data from the benchtop device resulted in RMSEC and RMSEP values of 0.009 wt% and 0.007 wt%, respectively (see Fig. S2).

The benchtop FT-NIR system outperforms the SCiO sensor with

Table 1

Diagnostics of the PLS regression models for the prediction of water concentrations in MEK (values in wt%).

Device (spectral region)	RMSEC	RMSEP
SCiO (740–1070 nm)	0.011	0.012
Bruker (1860–1930 nm)	0.009	0.007
Bruker (870–1070 nm)	0.013	0.101

respect to quantification of low water levels, which is to a large extent due to the presence of the strong water combination band ($\nu_{1,3} + \nu_2$) in the spectra of the benchtop FT-NIR system compared to the weaker second overtone of the O–H stretching band ($3\nu_{1,3}$) in the spectra of the SCiO sensor. However, when the systems were directly compared by using PLS regression only on the data from the 870–1070 nm spectral range (i.e., disregarding the rest of the benchtop range), the data from the FT-NIR benchtop instrument resulted in models with slightly worse RMSEC (0.013 wt%) and RMSEP (0.101 wt%) values than those obtained with the SCiO sensor (see Table 1). It appears that the $3\nu_{1,3}$ band at 980 nm cannot be positively identified in the FT-NIR spectra (Fig. S3), while the SCiO sensor seems to be optimized in this region. An additional factor may be that the modes of measurement were not the same for both devices: SCiO measurements were collected by transflection (optical pathlength 2 cm) and the FT-NIR spectra by transmission (optical path length 6.8 mm). The data from the handheld and benchtop device are available online for further analysis [16].

4. Conclusions

We have developed methodology for the successful application of the low-cost SCiO NIR sensor on transparent liquids, specifically organic solvents. The NIR spectral range of the SCiO sensor allows for 100% identification accuracy of selected solvents. The same accuracy may be achievable by using an even narrower spectral range (we welcome the interested reader to further analyze the available data). Moreover, low water concentrations can be quantified with this sensor with a precision of approximately 0.01 wt%. Together, these results demonstrate fit-for-purpose feasibility of low-cost NIR applications on liquids in a variety of industries and research fields, including QC applications at manufacturing sites where improvements in efficiency and sustainability will be achieved through deployment of the methodology that we have reported here.

CRediT statement

Geert van Kollenburg: Conceptualization, Methodology, Investigation, Formal analysis, Supervision, Project administration, Writing – Original draft, These authors contributed to the work equally.. **Henk-Jan van Manen:** Conceptualization, Funding acquisition, Methodology, Investigation, Formal analysis, Project administration, Writing – Original draft, These authors contributed to the work equally.. **Nicole Admiraal:** Methodology, Investigation, Formal analysis, Writing – Original draft. **Jan Gerretzen:** Methodology, Investigation, Supervision, Writing – Review and editing. **Jeroen J. Jansen:** Funding acquisition, Writing – Review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2020.121865.

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