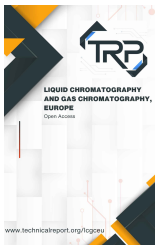

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RESEARCH ARTICLE

Range-Resolved Dual-Window Near-Infrared and Fiber-Tip Plasmonic Assessment of Water Content in Methanol-Rich Liquids

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Abstract
Quantitative water analysis in methanol-rich solutions represents analytical challenges in terms of broad, band-overlapping, and concentration-dependent near-infrared behavior of hydrogen bonding liquids and the nature of near-interface sampling by fiber-tip plasmon resonances. This study proposes a range-resolved approach for the quantitative interpretation of methanol–water samples based on combining two near-infrared absorbance regions with localized surface plasmon resonance tuning of a nanostructured optical fiber sensor. The main research problem is whether water fraction from 0 to 50% wt can be better analyzed when divided into different sensitivity ranges instead of integrating all three signals, such as absorbance at 1450 nm, 1950 nm, and plasmon red-shift wavelength, in a common calibration curve. Concentration values are organized into a ten-level composition series, which then are expressed through four analytical descriptors: normalized band area completion, signal increments at the first calibration range, band area ratio, and accumulated plasmon blue-shift value. As seen from the descriptor table, the contribution to absorption in the combination region at 1950 nm rises to 52.9% upon reaching 10 % water content, whereas absorption in the overtone region at 1450 nm reaches just 35.3% within this range. The LSPR center shifts from 1527.0 nm to 1504.2 nm, providing a total blue shift of 22.8 nm. The data confirms the effectiveness of using a range-resolved fusion scheme in this case. The reason is that water quantification in the lower ranges of interest is achieved due to the 1950 nm band, while the high range continuity is ensured through the overtone band at 1450 nm. Moreover, the plasmonic response provides independent verification of the interface conditions. Thus, the present analytical scheme is a useful tool for analyzing methanol-rich solutions in terms of their liquid chemistry and instrumentation specifics.

Keywords: near-infrared spectroscopy; localized surface plasmon resonance; methanol–water mixture; water determination; optical-fiber sensor; range-resolved calibration; analytical chemistry; liquid spectroscopy

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1. Introduction

Accurate quantification of water in organic solvents remains a challenging issue in analytical chemistry since moisture affects the selectivity of a reaction, efficiency of chromatography and extraction, preparation of pharmaceutical substances, and long-term solvent stability. Among various solvents, methanol deserves special attention as the popular component of the reagents, mobile phases, cleaning fluids, and solvents in general. Methanol is particularly difficult to analyze due to its perfect solubility with water. In addition, visual examination cannot be applied reliably as the quantitative method to determine the proportion between the pure solvent and water content. Thus, despite the availability of the gravimetric and optical techniques, Karl Fischer titration still plays a key role in many analytical approaches. Karl Fischer titration, however, is relatively wasteful, requires reagents, and cannot be applied repeatedly in-line with liquid flow or closed-loop systems [1–3]. Another option is optical spectroscopy that has advantages in terms of speed, non-destructiveness, and miniaturization.

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Near-infrared spectroscopy in particular is attractive for liquid analysis due to the absence of interference from the glass containers and compatibility with fiber-optics and mini-spectrometers.

Overtone and combination absorptions in near-infrared spectroscopy are relatively weak compared to fundamental mid-infrared peaks, which means that measurements can be done using practical path lengths and fiber components. Moreover, the capability of near-infrared measurements has been demonstrated for different applications, including process control, pharmaceutical studies, food science, agriculture, and solvents testing. At the same time, the weakness of near-infrared absorptions presents certain analytical problems. The near-infrared peaks tend to have a wide bandwidth; neighboring peaks often interfere, and different instrumental parameters such as path-length fluctuations, thermal shifts, baseline offset, instrument response variations, and fiber instability contribute additional artifacts. To obtain a reliable analysis, the approach needs to be cautious about interpreting each individual peak as the absolute measurement of concentration, especially considering the non-linear behavior at the high-concentration limit. As a result, the proper choice of both spectral window and instrumental setup should be based on the analysis of liquid absorptions in this specific wavelength range.

Water is one of the most significant near-infrared absorbers in routine analyses of liquid solvents. Due to the overtone and combination peaks, O–H vibrations produce broad absorptions, which depend on hydrogen bonds in the molecule. When combined with methanol in a solvent, water does not behave as a simple mixture of two pure absorptions. Thus, the region close to 1450 nm corresponds to the O–H overtone, while the region around 1950 nm represents a water combination absorption peak. Both windows are informative, but their utility depends strongly on the water content. The 1950 nm peak has a good sensitivity to low concentrations; its intensity, however, compresses at high concentration levels. In contrast, the 1450 nm region produces an absorption profile with a gentler behavior in the whole concentration range, albeit with a low intensity at low concentrations. As a result, any attempt to perform near-infrared analysis of methanol solutions has to account for the distinct features of each region [4–6].

The chemometric approach confirms the need for such an analysis. Preprocessing steps such as smoothing, derivative detection, and baseline correction are useful tools in near-infrared analysis because they help to distinguish real molecular peaks from instrumental artifacts. Nevertheless, these techniques require certain chemical care in selecting and explaining the relevant peaks. Thus, smoothing has to produce no artificial structure in the resulting spectra, while the preprocessed variable must have a physical meaning. The same is true for derivative analysis that highlights specific regions and eliminates unwanted signals. Therefore, chemometric analysis involves the selection of an adequate spectral window and the corresponding chemical meaning of the obtained results.

The combination of miniaturized spectrometers and fiber-based sensors creates new opportunities in near-infrared analysis. Small size, robust design, and compactness of such systems are beneficial characteristics compared to the traditional benchtop spectrometers, while fiber optics helps to couple multiple optical paths. The combination of bulk absorption and plasmon resonances of a metal surface is particularly useful in analyzing liquids, since the first channel probes the bulk liquid while the second channel responds to the surface properties. Near-infrared transmission and localized surface plasmon resonances present two very different approaches to measuring water in methanol.

Localized surface plasmon resonance refers to collective oscillations of electrons in metal nanolayers that lead to the optical resonance. Plasmons react to changes of the refractive index close to the metal surface and can respond to surface modifications or to the presence of adsorbed or interacting molecules. The ability of plasmonic analysis to detect changes at the surface, however, is a double-edged weapon. On the one hand, the response of LSPR sensors is valuable because it contains information related to surface modification and chemical composition near the metal surface. On the other hand, such information can be distorted by the surface characteristics or interfacial interactions between the liquid and metal layers. In liquids, hydrogen bonding may play a special role by affecting surface properties [7–9].

The main data source for this article is the analysis of the multiparametric near-infrared measurements of methanol-water mixtures using an optical-fiber arrangement described previously by Delli Santi et al. [10]. This paper answers the following question: can the water concentration in a solution be characterized using a range-resolved descriptor fusion rather than a single band intensity or resonance shift? To find the answer, one needs to explore the relationship between water concentration and band sensitivity; describe the compression of the peak at high concentrations; assess the migration of plasmon resonances.

The novelty in this work consists of three parts. First, the concentration descriptors are normalized, transformed into incremental values, and presented in the table form, allowing one to identify the regions of maximum sensitivity and compression. Second, the specific functions of all optical channels are assigned based on the sensitivity analysis. Specifically, the absorption in 1950 nm acts as a low-concentration sensitivity descriptor, the absorption in 1450 nm works as a range-stable absorption descriptor, while the LSPR center indicates the interfacial consistency of the sample. Third, each table and figure below is explained in detail, without references to the equations and derivations; the text focuses on the analysis of optical results.

This paper aims to investigate the water content in methanol by optrode-assisted near-infrared analysis. This analysis is based on near-infrared absorption, bulk optical path, and localized surface plasmon resonances. Thus, the manuscript represents a near-infrared spectroscopy study for determining water in methanol solutions.

2. Materials and Methodology

2.1. Measurement basis and descriptor construction

In this study, the investigated concentration range includes methanol solutions with water concentration from 0 to 50 % w/w. To characterize the liquid, near-infrared spectra were collected in the wavelength region of approximately 1200 nm to 2000 nm. The integral areas of absorption in two water-sensitive regions close to 1450 nm and 1950 nm were also measured. In addition, the central wavelength of the localized surface plasmon resonance was identified. Refractive index at 1550 nm was included only as a physical parameter of the liquid and does not influence the plasmon response, which can be considered as the near-interfaced optical property.

Range-resolved descriptor fusion is a suitable analytical tool to investigate a hydrogen-bonded liquid with concentration-dependent absorption. Thus, low-concentration region will be evaluated by early sensitivity of descriptors, middle region will be analyzed by the stable progression along the concentration scale, while high-concentration region will be described by the capacity of descriptors to discriminate between samples.

The scheme in Fig. 1 shows the sequence of optical components necessary to perform a measurement. The schematic presentation is necessary for understanding the stability of the whole optical chain, which determines the reliability of all descriptors regardless of the further calculation steps. The fiber coupling, alignment of the cuvette, emitter, and detector response are all factors that contribute to the stability of the measurements.

The scheme in Fig. 2 shows the optical region producing peaks at 1450 nm and 1950 nm. These peaks correspond to the absorption in the bulk region of the liquid. It is important to understand that the two types of measurement are distinct in the sampling volume.

Finally, the probe shown in Fig. 3 is a surface-probe device, i.e., the

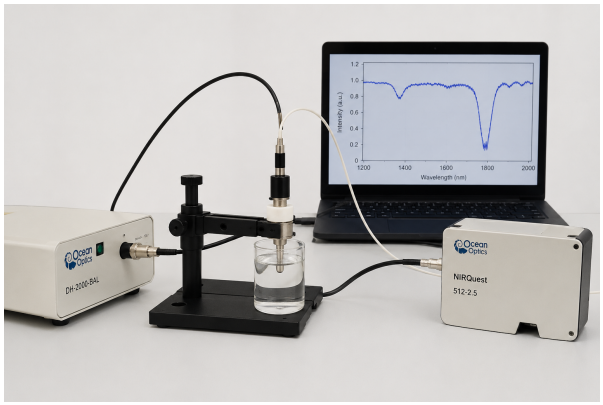

Figure 1: Instrument layout.

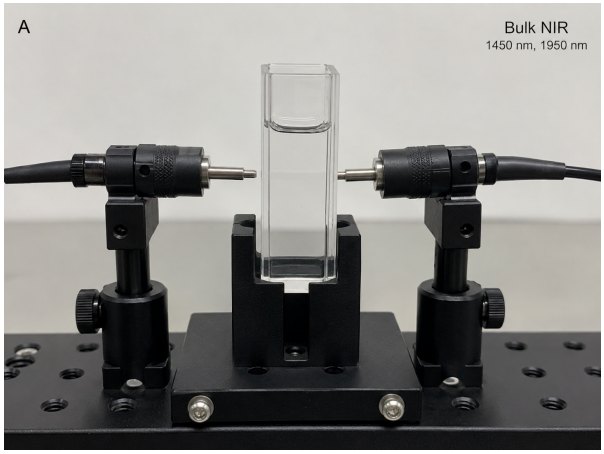

Figure 2: Bulk transmission path.

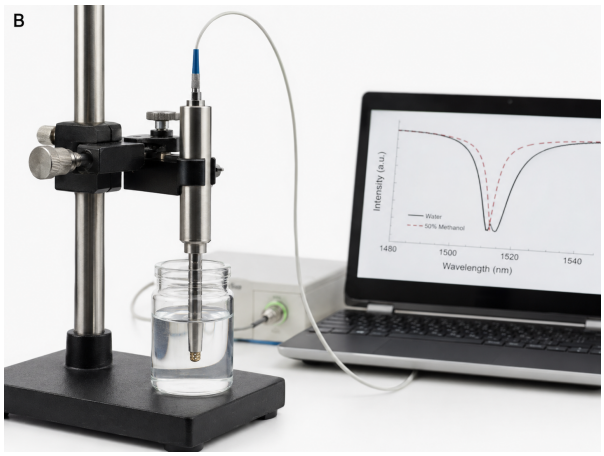

Figure 3: Fiber-tip probe.

light interacts with the liquid close to the surface. Therefore, the localized surface plasmon resonance in the fiber-tip is a response to interfacial properties of the liquid, not the bulk absorption.

The descriptors in Table 1 outline a technique using analytical sensitivity based on an analyte's effect on a function as opposed to its effect on the intensity of a signal. The absorption bands are kept in place due to their complementing information content, and the plasmonic variable is kept because it provides a different type of response. This is helpful when transferring techniques to other instruments that will use different optical setups as all of the descriptors' functions can be maintained.

2.2. Concentration series and derived descriptors

The first table contains the concentration variables used during analysis. The second table is obtained from these values, and includes normalized contribution of each band response, total LSPR blue shift, and the proportion of the two bands' areas. The new set of variables is not merely a cosmetic adjustment but an entire change in focus.

The results presented in Table 2 indicate monotone behavior for all descriptors, but this fact alone does not constitute an argument in favor of calibrating the series. While the 1950 nm peak area varies abruptly during the first two steps, the 1450 nm peak area varies more smoothly. Similarly, the LSPR coordinate decreases monotonically; however, the extent of such variation should be regarded as a parameter sensitive to the surface conditions.

The key point revealed by derived descriptors in Table 3 is that, at 10% water content, the 1950 nm band has already passed its mid-range peak point, while the 1450 nm band reaches approximately one third of its terminal response point. Band ratio also tends to decrease after reaching its maximum value. Thus, it is clear that the stronger combination band cannot serve as a unique guide throughout the whole range. The cumulative blue shift of LSPR can be viewed as an independent monotonic descriptor, the interpretation of which is dependent on the interface properties.

2.3. Spectral-window treatment

As usual for near-infrared applications, reference spectra are inspected in the methanol-dominant state to choose the right spectral window for analysis. Smoothing is acceptable solely in terms of noise reduction, since water absorption bands are sufficiently broad compared to spectral interval. As an additional verification procedure, derivative-based window choice is employed; the idea behind this is simple—selected windows should reflect the true shape of water-related absorption band and not the slope of spectral curve due to spectral offset or random fluctuation of noise level.

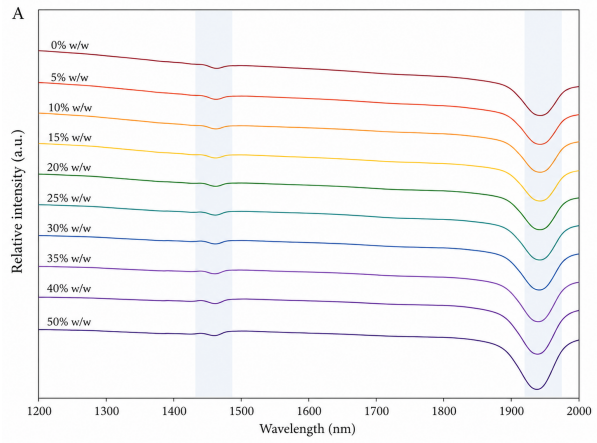

Figure 4: Full NIR spectra.

Inspection of the spectral family presented in Fig. 4 demonstrates that the water addition changes the overall spectral shape, i.e., the whole NIR range rather than generating a narrow band. It means that window integration is appropriate here, as it allows extracting more information about the analyte from water sensitive regions. Furthermore, the ordered increase of absorbance values proves that spectra can be used for interpreting water content. Different shapes of the major water absorbing regions indicate that one band cannot be employed to cover the whole range.

Examination of the magnified 1450 nm window presented in Fig. 5 reveals continuous growing behavior. It means that the overtone window

Table 1: Core optical descriptors.

Descriptor	Measurement domain	Analytical role in this study
Water fraction	Liquid composition	Defines the 0–50% w/w calibration interval and the three response zones.
1450 nm band area	Bulk near-infrared absorption	Provides gradual, range-stabilizing concentration information.
1950 nm band area	Bulk near-infrared absorption	Provides high early sensitivity and reveals compression at higher water levels.
LSPR center	Fiber-tip plasmonic response	Provides an interfacial optical consistency check independent of band intensity.
Apparent refractive-index scale	Physical reference	Supports cautious interpretation of the LSPR channel without treating it as a direct refractometer.

Table 2: Concentration-response values.

Water content	1450 nm area	1950 nm area	LSPR center (nm)	Index scale
0%	0	0	1527.0	1.3174
5%	11	42	1525.4	1.3173
10%	18	82	1523.1	1.3172
15%	24	104	1520.4	1.3172
20%	29	118	1517.5	1.3171
25%	34	128	1514.6	1.3170
30%	39	137	1510.7	1.3168
35%	43	143	1507.2	1.3167
40%	47	149	1505.7	1.3166
50%	51	155	1504.2	1.3166

Table 3: Derived response descriptors.

Water	1450 nm comple-tion	1950 nm comple-tion	LSPR blue shift	1950/1450 ratio	Analytical zone
0%	0.0%	0.0%	0.0 nm	–	Reference
5%	21.6%	27.1%	1.6 nm	3.82	Early
10%	35.3%	52.9%	3.9 nm	4.56	Early
15%	47.1%	67.1%	6.6 nm	4.33	Transition
20%	56.9%	76.1%	9.5 nm	4.07	Transition
25%	66.7%	82.6%	12.4 nm	3.76	Transition
30%	76.5%	88.4%	16.3 nm	3.51	Upper
35%	84.3%	92.3%	19.8 nm	3.33	Upper
40%	92.2%	96.1%	21.3 nm	3.17	Upper
50%	100.0%	100.0%	22.8 nm	3.04	Upper

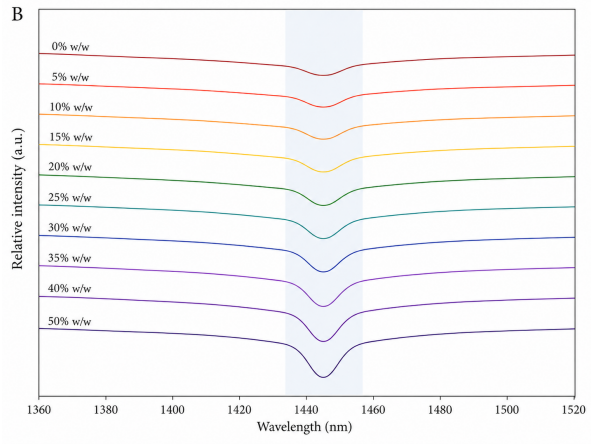

Figure 5: 1450 nm window.

has the ability to provide discriminative power over the whole investigated interval, which is due to moderate growth rate of absorbance. However, the fact that overtone window has a smaller absorbance signal compared to combination one does not influence its usability negatively.

Zooming the 1950 nm window presented in Fig. 6 leads to conclusion that this window has the biggest absorbance value for low water content, which is favorable in case of small amounts of analyte in

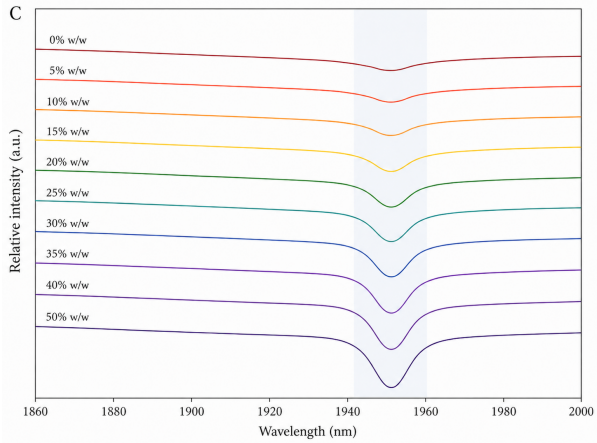

Figure 6: 1950 nm window.

methanol rich liquid. On the other hand, such strong response limits the possibility of water content evaluation using this window at higher water concentrations.

3. Results and Discussion

3.1. Behavior of two absorption windows in the whole range

The comparison of the response of the two absorption windows consists of two parts—comparison of cumulative growth and individual growth between subsequent intervals. The cumulative 1950 nm descriptor value increases from 0 to 82 relative units up to 10% water content, while 1450 nm descriptor grows from 0 to 18 relative units within the same interval. Further examination of the next interval—from 25% to 50% water content—shows that 1950 nm and 1450 nm descriptors add respectively 27 and 17 units. As a result, the difference between descriptors decreases rapidly.

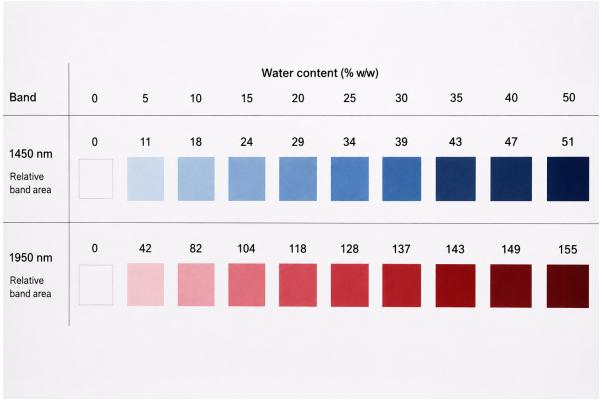

Figure 7: Band-area comparison.

Comparison of bands in Fig. 7 emphasizes the complementary nature of two bands. The crucial question for further analysis is not which band area is bigger, as the answer will always be—it is the 1950 nm

band. Therefore, the question is whether one or another band has information capacity in the current range segment. Detection of low water content requires a more sensitive signal, while coverage of the whole range needs stability of the response.

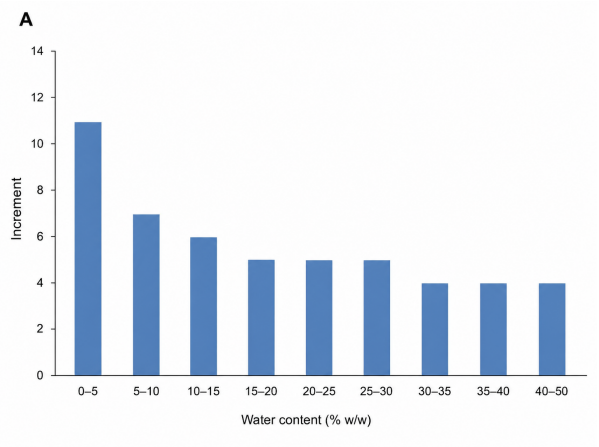

Figure 8: 1450 nm increments.

Inspection of the interval profile of 1450 nm descriptor increment (Fig. 8) confirms that this descriptor is suitable for broad range analysis, especially when the amount of analyte is enough to approach combination band saturation. Decreasing of absorbance increments at the last stages of the process proves the existence of this tendency.

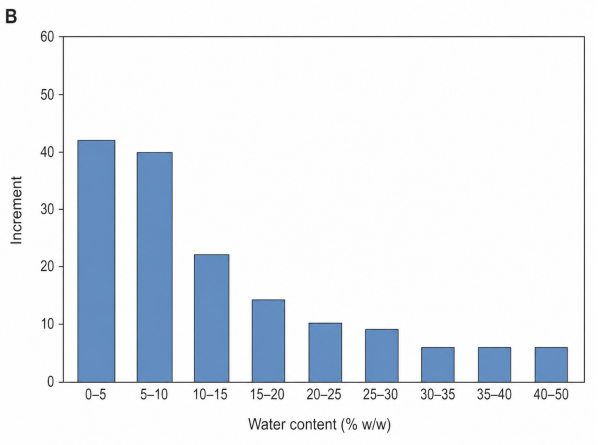

Figure 9: 1950 nm increments.

The 1950 nm absorbance increment interval profile (Fig. 9) highlights a specific feature that limits the applicability of this descriptor. Namely, the fact that two first increments dominate over the remaining ones indicates the necessity to weight this band in case of low water content and avoid its usage for evaluating samples with a higher water content proportionally.

The normalized trajectories in Fig. 10 show that the three descriptors do not mature at the same rate. The 1950 nm band advances fastest in the early zone, the 1450 nm band follows a more even progression, and the LSPR blue shift accelerates most strongly through the middle and upper portions of the sequence. This non-identical maturation is the strongest evidence for descriptor fusion: the channels are related to water content, but they are not redundant.

Zone logic for the spectrum in Table 4 transforms the concentration trends into a practical analytical strategy. The concentration interval is divided into zones that have their own signal hierarchy, hence the calibration rationale should be non-uniform for the entire range of 0-50%. This is what the paper offers as its analytical contribution to

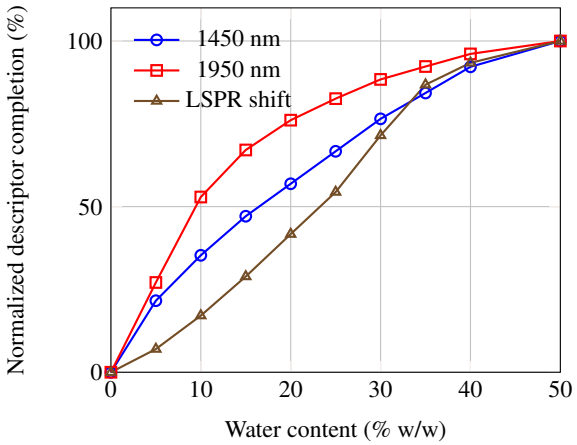

Figure 10: Normalized descriptor trajectories.

solving the task at hand: the plot of the concentration-response table should not just be presented, it should be converted into an analytical scheme defining the role of each optical channel.

3.2. Monotonic blue shift of plasmonic resonance and its interfacial character

LSPR center shifts towards the shorter wavelengths monotonically as the water amount increases. The center is approximately 1527.0 nm at 0% of water in methanol solution and approximately 1504.2 nm at 50% water, leading to a blue shift equal to 22.8 nm. This is helpful in analyzing the problem because the shift is ordered within the concentration series, but it cannot be regarded as a bulk refractive index measurement as such. The corresponding changes in refractive indices are negligibly small in comparison with a significant shift caused by the LSPR position alteration.

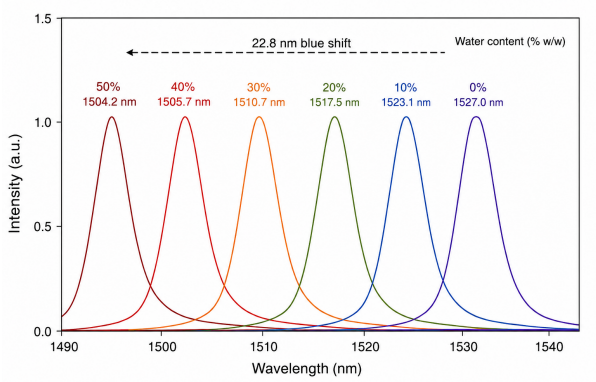

Figure 11: LSPR blue shift.

This LSPR shift pattern enhances the effectiveness of the method in the sense that it provides an interfacially consistent signal in addition to absorbance bands. An increase in the absorption signals in both windows should correspond to the LSPR position change. The lack of coherence in the response of the LSPR and absorbance descriptors should raise concerns about the presence of fouling on the surface of the nanostructured fiber, temperature variations, or the presence of an instrument error. The plasmonic response is therefore most useful as a consistency signal.

From the results of plotting incremental responses shown in Fig. 12, it becomes clear that while the 1950 nm feature is exceptionally good in providing information in the early phase of water addition, it starts losing its ability of discriminating between concentrations as the con-

Table 4: Response-zone interpretation.

Water interval	Dominant signal behavior	Main analytical risk	Preferred interpretation
0–10% w/w	Rapid 1950 nm growth and early LSPR movement	Overweighting the strongest band may exaggerate linearity	Use 1950 nm for sensitivity, check with 1450 nm and LSPR consistency.
10–25% w/w	Both bands remain ordered; LSPR shift becomes stronger	Treating all descriptors as equivalent may obscure response curvature	Combine both bands and monitor plasmonic movement as an independent channel.
25–50% w/w	1950 nm increments narrow; 1450 nm retains discrimination	A single strong band may under-resolve upper-range differences	Give more interpretive weight to 1450 nm and use LSPR as a consistency descriptor.

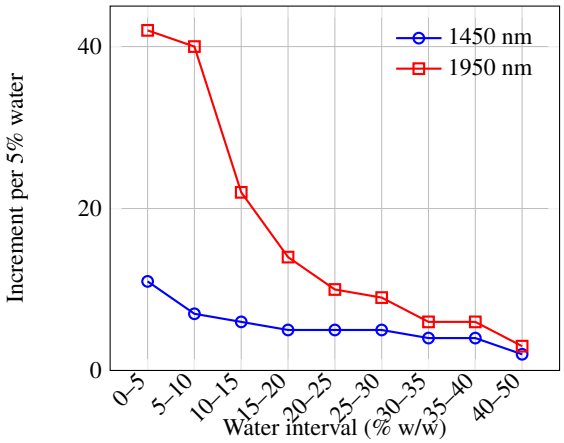

Figure 12: Incremental band sensitivity.

centration grows. On the other hand, 1450 nm features remain informative throughout the entire concentration range. Thus, a distinction needs to be made between the descriptors for the early zone and the later ones.

3.3. Integrative readout procedure

An efficient water determination protocol should be simple enough to allow implementation in a portable system and constrained enough to avoid misleading conclusions. Based on the findings reported above, a practical integration scheme can consist in first checking the overall spectral signature, and then examining the 1450 and 1950 windows, calculating area descriptors for these windows, recording the LSPR peak position, and comparing these descriptors against range-resolved expectations. The point here is not to complicate the analysis unnecessarily. The goal is to prevent using early water sensitivity as a universal predictor.

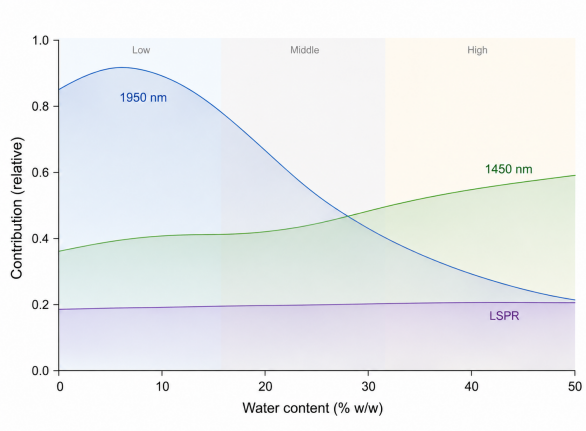

Figure 13: Signal contribution map.

The role of each channel in the analysis is schematically summarized in Fig. 13. While absorbance in the windows indicates the chemical identity of the liquid, i.e., the presence of O–H bonds, the LSPR shift provides independent evidence about the interfacial environment changing along with water additions. The advantage of the contribution map is that it prevents an integrative protocol from degenerating into a mere collection of spectral plots.

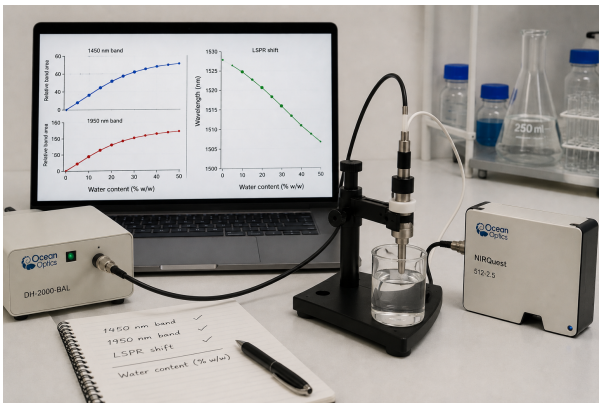

Figure 14: Integrated readout.

In Fig. 14, the readout protocol is depicted with respect to the conditions typical of a compact analytical system. This protocol does not focus on one of the windows alone, but combines information from the near-infrared envelope, absorbance windows and LSPR position into one coherent picture, allowing reporting water content and diagnostic information simultaneously.

3.4. Comparing with one-channel interpretation

An integration strategy can be simplified to the use of a single optical channel, but the effectiveness of this strategy will be reduced. In case only the 1950 nm window is considered, the technique will exhibit high responsiveness in the early stage of water concentration and low responsiveness in the late stage. If only the 1450 nm window is used, high responsiveness will be preserved but the early responsiveness will be lost. In case of a single channel consisting of the LSPR position alone, a reliable water response will become problematic, as well as the possibility of obtaining evidence about the composition of the liquid based on absorbance.

The advantage of the combination of both absorption windows and LSPR position is in the following: while the 1950 nm band is utilized for detecting early stages of water addition and the 1450 nm band ensures stable behavior at high concentrations, the LSPR center monitors whether the interfacial environment at the tip of the fiber changes consistently. This conclusion about the necessity of sensor fusion does not emerge without justification: it is supported by results in tables 2–4 and Figs. 5–12.

3.5. Implications for calibration and validation

According to the described descriptor logic, the following steps should be taken to develop a calibration protocol: obtain independent replicate spectra of water-methanol solutions at different compositions, control the measurement conditions, verify results using Karl Fisher method, assess repeatability and accuracy at different water concentrations, and test recovery for unknown samples containing methanol and water. Separate validation of calibration should be performed for each zone independently, as each zone exhibits distinct signal behavior. The average prediction error cannot provide sufficient calibration quality information.

In terms of instrumental design, it is recommended to prioritize 1950 nm band for determining low water concentrations, and to pay attention to choosing appropriate path length and ensuring the absence of dynamic range overload for the high water range. Finally, for fiber-tip analysis, special considerations need to be given to the issue of reproducibility. This includes fiber-cleaning procedures, interfacial measurements, and control measurements for assessing the refractive index of the solvent [11–13].

3.6. Limitations

First, the available data consists of the list of calculated concentration-response coordinates, and figure-level spectra only, i.e., no replicate spectra obtained from independently prepared samples. As a result, the paper concludes in the discussion by offering a strengthened analytical interpretation of the data and an approach to validation; however, a complete analysis of measurement uncertainty cannot be provided without replicate raw spectra.

Secondly, the physical origin of the plasmonic center shift is somewhat ambiguous, even though it is known that the shift occurs monotonically within the entire range of concentrations. The blue-shift effect may originate from both bulk refractive index and interfacial solvent environment; therefore, the safest conclusion is in treating the LSPR response as a consistency measure.

Thirdly, while the described methodology is applicable for 0-50% concentration range, it cannot be used directly to analyze samples with higher water concentrations. Furthermore, in case different solvents are used for testing this method, the behavior of descriptors is expected to change due to differences in hydrogen bonding capabilities and absorbance properties.

4. Conclusion

Based on the results described in the introduction section, the hypothesis that a combination of two near-infrared bands and plasmonic resonance position can enhance the water measurement effectiveness compared to the use of a single optical signal was investigated. It was concluded that the 1950 nm band responds effectively to early water additions by reaching 52.9% of its ultimate value already at 10% of water, while the 1450 nm band reaches 35.3% in the same time period, but continues to discriminate successfully at higher concentration values. Finally, the plasmon resonance position shifts monotonically from 1527.0 nm to 1504.2 nm as the percentage of water in methanol goes from 0 to 50%.

In this connection, the paper provides a definite answer: a combination of the two bands and the LSPR peak position can improve the water content estimation in methanol-rich solutions as compared with the traditional single-channel analysis. Specifically, the 1950 nm window can be used to determine low water concentrations due to early sensitivity, while the 1450 nm window can be used to obtain a broad-range trend. The plasmonic peak position will verify the consistency of the analysis.

As such, a combination of both absorption bands and plasmonic resonance position appears effective as a tool for compact analytical spectrometry of methanol–water solutions in the range of 0-50% concentration. This approach provides a complete concentration response table, a distinct signal descriptor hierarchy, concentration zone division, and a clear conclusion derived from the descriptor behavior. In order to develop a quantitative method from there, it needs to be validated with replicate measurements and temperature/path-length controls.

Data Availability

The concentration-response values and derived descriptors used for analysis are listed in Tables 2 and 3.

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