

On-Site Analytical Tool Based on Crude Oil Fluorescence and Chemometrics for the Rapid Determination of the Nature and Essential Properties of Oil Spills

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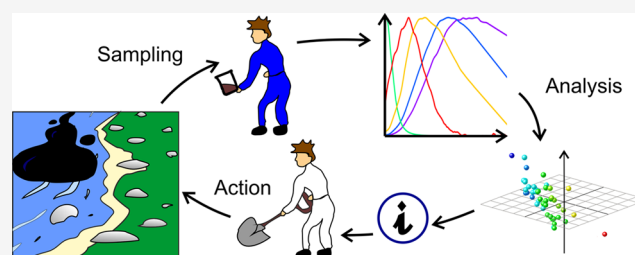
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ABSTRACT: With the reduction of large oil spills because of stricter regulations and safety measures, the question of how to manage smaller oil spills arises. Few on-site analytical tools are available for first responders or other law enforcement personnel to rapidly test for crude oil in the early management of localized polluted areas. The approach reported here relies on well-described computer-assisted multivariate data analysis of the intrinsic fluorescence fingerprints of crude oils to build a multivariate model for the rapid classification of crude oils and the prediction of their properties. Thanks to a dedicated robust portable reader, the method allowed classification and accurate prediction of various properties of crude oil samples like density (according to API, the American Petroleum Institute) and viscosity as well as composition parameters such as volume fractions of paraffins or aromatics. In this way, autonomous operation in on-site or in-the-field applications becomes possible based on the direct (undiluted and untreated) measurement of samples and a rapid, tablet-operated readout system to yield a robust and simple analytical test with superior performance. Testing in real-life scenarios allowed the successful classification and prediction of a number of oil spill samples as well as weathered samples that closely resemble samples collected by first responders.

KEYWORDS: oil spills, fluorescence, PCA, petroleum, rapid test, portable



INTRODUCTION

Thanks to environmental policies, including the creation of international structures for environmental monitoring of the oceans and seas, the number of massive oil spills has steadily decreased over the last 30 years. However, together with this reduction, the question of managing smaller oil spills has gained more importance.¹ High-level technologies used to detect spills all around the world such as the Copernicus program deployed by the ESA,² on-board LIDAR systems installed on planes,³ or the radar systems placed on sea platforms are either dedicated to global surveillance or are costly solutions.⁴ For smaller, more localized oil spills in the oceans and seas, but also in lakes or rivers, only few on-site analytical tools are available to ensure a proper management of the depollution.^{5–7} Indeed, small oil spills are more difficult to track as well as often more challenging to depollute, especially when appearing in less accessible areas.

The detection of suspected oil spills in unknown contamination scenarios commonly relies on the intrinsic properties of crude oils. Several techniques can be used for such purposes, most of them complying with the standard methods established by the American Society for Testing and Materials (ASTM) International or the American Petroleum Institute (API). These methods are often complex, time-consuming, and expensive, involve toxic solvents in the

processes, and require bulk sample quantities. Therefore, the development of analytical tools affording important information about petroleum-related properties and the nature of the oil spills in a more user-friendly and cost-effective way is of great interest, especially for small-scale scenarios.^{8–10} Perhaps the most obvious parameter is the oil density or API classification, which is frequently used by the petroleum industry because it provides information related to the production, refinement, distribution, pricing, and toxicity of oils. Crude oils with a high °API contain a higher percentage of hydrocarbons that can be recovered by simple distillation; however, they are considered the most toxic. The density of the oil relative to the density of water will determine the position of the spill in the water column or the downstream transfer distance in the case of a river. Another physical property that is very useful for oil characterization is its viscosity (kinetic or dynamic). It can vary from a low-viscosity

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liquid to a tarlike, nearly solid form and will influence the oil's dispersibility.¹¹ Such parameters would, for example, be crucial to select the skimmer type to clean water bodies from oil contamination.¹²

Many efforts to develop new techniques have been made in the last years, often based on fluorescence spectroscopy and multivariate analyses of the oil's fingerprints obtained from excitation–emission matrices (EEM).¹³ Such techniques, similar to those reported for gas chromatography,¹⁴ mass spectrometry,^{15–17} or infrared spectroscopy^{18–20} studies, rely on the complex and unique mixture of each crude petroleum or fuel and their unique fluorescence fingerprint. Many reported studies showed the possibility to detect and identify crude oils by recording the direct fluorescence emission of oils upon ultraviolet (UV) excitation^{21,22} without any pretreatment and by comparing the results to a prerecorded library by means of principal component analysis (PCA).

Here, aiming at on-site measurements, a hand-held analyzer incorporating a miniaturized spectrometer for fluorescence emission measurements was devised, communicating wirelessly with a mobile device such as a tablet for operation, data retrieval, and chemometrics analysis. As reported in the literature,²³ the measurement of fluorescence spectra allows us to classify oil samples and to extract saturate, aromatic, resin, and asphaltene percentages (SARA);²⁴ however, the additional prediction of physical data of the sample, such as density or viscosity, which tremendously helps in taking first action toward depollution has been realized here for the first time. This combination was tested on oil spill samples, weathered samples, various oil–water mixtures (mousses), and sediment–oil aggregates to validate the method for rapid on-site testing in case of localized oil spills and to provide immediate access to critical parameters for hazard assessment and depollution.

■ EXPERIMENTAL METHODS

Spectrometer. Reference spectra were acquired using steady-state fluorescence measurements carried out in front face configuration on a Cary Eclipse spectrofluorometer (Agilent Technologies, Santa Clara), the pure oils having been deposited directly in standard quartz cells of 10 mm path length without further treatment.

Portable Analyzer. The portable analyzer, as described in detail in a previous study,²⁵ is built around two different electronic subsystems (Figure S4): a permanently operating part for power supply management including a Hall-effect sensor (magnetic ON/OFF switch), a USB rechargeable lithium polymer battery with a charging capacity of 2 Ah, and a power controller board (PCB). The second subsystem contains components such as the microcontroller, the spectrometer, the LED, and the Bluetooth module. An ARM Cortex M4 microcontroller, programmed with C/C++, was used to drive the spectrometer and to achieve the first data treatment before sending the data via Bluetooth LE or USB connection to the evaluation unit for data reception and analysis (tablet or PC). The light source for the excitation of the samples was an LED with an emission wavelength of 310 nm focused through a fused silica half-ball lens on the sample. A holder that can accommodate a quartz beaker in which the sample (up to 5 mL of oil) is filled was three-dimensional (3D)-printed from acrylonitrile–butadiene–styrene (ABS) filaments to fit on the optical window of the device. The pure oil samples were poured directly, without further

pretreatment, into a quartz beaker with a flat bottom, and the fluorescence emission of the samples was then collected through a diffraction slit of a microspectrometer (range: 323–813 nm with 256 bits resolution, C12666MA Hamamatsu) using an aspheric lens, amplified with a differential amplifier, and sent to the evaluation unit. To improve the signal quality of the spectrum, the digital and analog components were strictly separated. An additional shielding of the analog signals and components was introduced on the PCB to provide additional protection against electromagnetic interference.

Data Set and Multivariate Studies. Various data sets were compiled from the reference spectra or the portable analyzer spectra with or without including external spectra found in existing databases. The full data set lists 92 entries of emission spectra, including 49 crude oils (including 3 oil spills) (Table S1), 4 heavy fuels (including 1 oil spill), 16 refined fuels (including 1 oil spill), 9 lubricating oils, 1 grease, 3 biogenic oils, and 10 vegetable oils. Some of the spectra were downloaded directly from a database of Oldenburg University, which had been compiled during the Science Education through Earth Observation for High Schools (SEOS) Project.²⁶ This database comprises 59 samples with excitation wavelengths of 310, 340, or 365 nm and emission from 320 to 690 nm. In addition, real-life samples were prepared: 4 weathered samples of Arabian light crude oil, 2 mousses from the mixing of surface and seawater with Oseberg crude oil, and 1 sediment sample also prepared from Oseberg crude oil. The spectra collected with the fluorometer or the portable analyzer were truncated to fit the wavelength range from 320 to 690 nm of the Oldenburg University spectra. The data set was built by compiling these spectra, in a tabulated Excel file (Microsoft) including oil reference and wavelength range data. The only data processing consisted of normalization to 1 using OriginLab software (OriginLab, Northampton). All the spectral data sets were fed separately into the multivariate analyses algorithm to check for best PCA resolution and accuracy. Sample spectra noncompatible with the method were nonfluorescent oil samples like asphalt or purified polybutenes. Such outliers were therefore not included in the data set, especially because they present low threats in terms of oil spills. PCA was performed using the Principal Component Analysis (v1.50) in-app program of OriginPro 2022 (OriginLab) to trace the variations of fluorescent components and identify oil properties. While the oil's properties used in the data set are known, the predicted parameters can be directly compared for validation. Integrated full cross-validation with leave-one-out cross-validation (LOOCV) was utilized to validate the output from PCA analyses of the compiled databases.^{27,28}

■ RESULTS AND DISCUSSION

Multivariate Analyses. A large variety of samples with heterogeneous properties, composition, and origins were collected to avoid method bias and ensure robustness of the method. Most samples were crude oils and heavy and refined fuels as they are the most probable source for oil spills. Together with these samples, other oils such as lubricating oils, greases, and nonconventional synthetic oils were also integrated into the data set to reinforce our statistical analyses. The latter are produced in lower quantities and are therefore less likely to lead to oil spills, but they are nonetheless toxic and dangerous for the environment. As relevant potential interferents and to include variability in the data set, biogenic oils, i.e., fish and vegetable oils, which are nontoxic natural oils,

but which are often also autofluorescent, were additionally integrated into the data set. No pretreatment was performed on the samples and only a reasonable quantity (1–5 mL) was poured into a spectroscopic quartz cuvette or a quartz beaker. The oils' emission spectra were measured with a conventional fluorometer to determine the optimum excitation and emission parameters for multivariate analyses. The crude oils and all of the derivatives obtained from petroleum showed typical broad emission bands in the ultraviolet/visible spectral range upon UV excitation, mostly due to the presence of polycyclic aromatic hydrocarbons (PAHs).²⁹ For biogenic and vegetable oils, autofluorescence can stem from polyphenols, riboflavin, chlorophyll, vitamins, or even PAHs in case of contaminated fish oil.³⁰ Limitations of the method were noticed for synthetic oils like polybutenes and poly α -olefins that are not fluorescent and therefore not detectable by a fluorescence-based method. Similarly, extremely viscous crude oils and oil derivatives, such as oil sands or asphalt, exhibit low or virtually no fluorescence, preventing detection by the developed method.

As reported previously,³¹ the combination of oil emission spectra and chemometrics allowed for classification of the different oil types. From measurements conducted in the laboratory, optimum parameters for building a portable analyzer were extracted. The spectra obtained with the analyzer were similar to those obtained with a conventional fluorometer (Figure S5) and thus yielded results of similar quality when submitted to multivariate analyses (Figure 1).

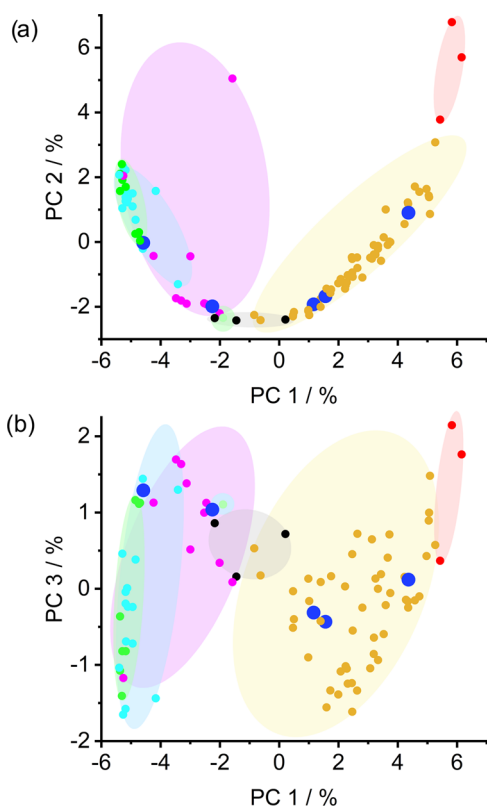


Figure 1. (a, b) PCA scores obtained from spectra data set at 310 nm. Black dots, biogenic oils; red dots, heavy oils; light blue dots, refined petroleum products; green dots, lubricating oils; purple dots, vegetable oils; golden dots, crude oils; turquoise dot, grease; big blue dots, oil spills (center of probability ellipses at barycenters of the points belonging to the same cluster, and the main axis explaining the maximum of variance).

From the scores, three clearly separated families can be distinguished: a cluster of native crude oils, a cluster of refined petroleum products together with vegetable and biogenic oils, and a small cluster of heavy fuels. The coefficients of the components (Figure S6) show that the components are strongly related to the wavelength ratios between the UV, blue, and green ranges of the spectra compiled in the database. The resulting PC1/PC2 score plot hence exhibits an alignment of the various oils on a parabola-like feature with the distribution of PC1 scores from light oils to heavy oils and PC2 scores separating the light oils from the vegetable and biogenic oils and the medium oils from the heavy oils. In addition, the PC1/PC3 score plot shows that PC3 favors a spread of the individual clusters, affording a better resolution between the same types of oils.

Among the spectra of the data set, five are from oil spill samples and therefore without known parameters or families, but still those are processed in the principal component analysis like the other spectra of the known samples and downloaded data sets (Figure S7). One sample is from the Archimedes II experiment reported as Ekofisk crude oil (Figure S8A),³² three are from samples used for exercises of the International Convention for the Prevention of Pollution from Ships (MARPOL), reported as similar to Statfjord crude oils and diesel (Figure S8B–C);²¹ and one sample is from a IFO380 pipe leak in the Donges refinery in 2008 (Figure S8D).³³ From the spectra, the MARPOL samples are indeed close to the Statfjord crude oil, but for the Archimedes II sample, the spectrum is much more shifted to the red compared to Ekofisk, being spectrally closer to heavy crude oils like Gach Saran (IRN), Romaschkino (RUS), or Tuymazy (RUS). Nonetheless, it can be seen from the PCA scores that the two crude samples of the MARPOL exercise and the sample of the Archimedes II experiment are perfectly included in the crude oil cluster. In the same way, the third sample from the MARPOL exercise is included in the cluster of refined petroleum products in accordance with the exercise reports, indicating light diesel fuel as a pollution material. The last sample does not fit into a cluster but is between those corresponding to refined petroleum products and crude oils. Indeed, this last sample is a high-viscosity ($380 \text{ mm}^2 \text{ s}^{-1}$) intermediate fuel oil (IFO), a blend of heavy fuel oil and lighter fuels. Its hybrid nature is reflected by its position between two clusters. Noteworthy, the spectra of another IFO with low viscosity ($180 \text{ mm}^2 \text{ s}^{-1}$) are included in the data set, yet the sample containing a much lower content of light fuels is correctly classified in distinctly closer vicinity to the heavy fuel cluster.

Extracting Crude Oil Parameters. To further interpret the crude oil properties, the data set was reduced exclusively to the crude oil spectra before submitting to multivariate analyses (Figure S9). Interestingly, PC1 appeared to be strongly dominant and related to the emission band maxima of the oils; indeed, its coefficient is almost linear with wavelength. The fluorescence spectra of the crude oils, especially the shift of the emission bands to the red, are known to be related to aggregation or π -stacking of the PAH species present in petroleum products to form excimers as dominant emitting species.^{34,35} This bathochromic shift induced by π -stacking of the aromatic rings is usually correlated to an increase in concentration of the fluorescent species but also to macroscopic properties such as viscosity and density for highly viscous media.

As the spectral data set of crude oils can be classified by multivariate analyses, some of the parameters of crude oils can be derived from their spectral signature when PLSR is applied to the data sets, allowing for statistical analysis (Figures 2 and

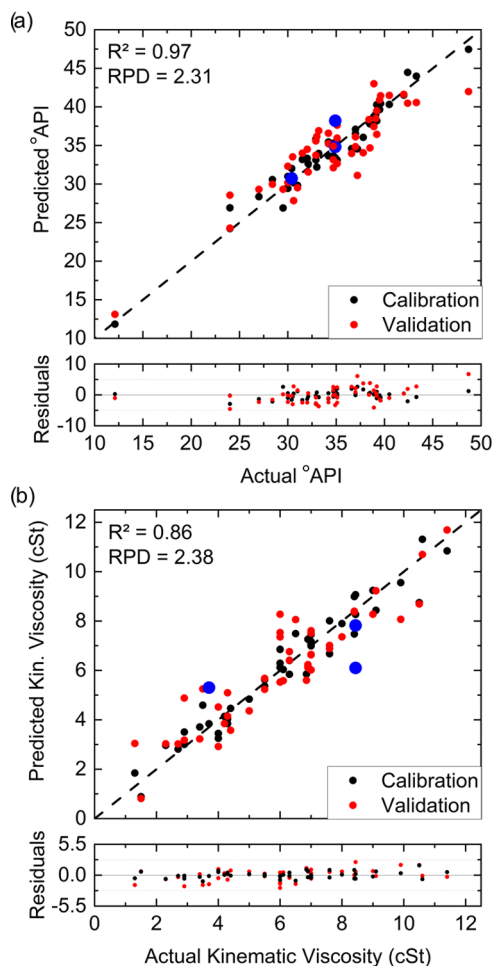


Figure 2. Partial least-squares predictive models for (a) °API and (b) kinematic viscosity from raw spectra of crude oils. The graph shows the correlation between measured and predictive values.

S10). For the calibration and validation sets, all samples from the data set with known characteristics (API, kinematic viscosity, etc.) were used to compute model components for each characteristic (Figure S7). Except for the H₂S content, the obtained prediction plots for the calibration of the models showed good linearity with R² ranging from 0.86 to 0.97. Also, except for the H₂S content, the residuals showed no trend but only random errors. The validation plots showed a strong deviation from linearity between actual and predicted values for H₂S, wax, and naphthalene content, but for aromatics, paraffin content, as well as API and kinematic viscosity, the prediction appeared to be more accurate.

To validate and estimate the prediction errors of the method, full cross-validation with leave-one-out cross-validation was utilized.^{36,37} For this validation procedure, the same spectral samples were used for the calibration and validation of the models. For each run, the value of the left-out sample was predicted, and the residual was calculated from the known characteristic. This process is repeated until every sample has been left out once, and the combination of all residual

parameters estimates the relative percentage difference (RPD)³⁸ and the determination coefficient of validation (R²),³⁹ (Table S3). To determine whether the results of multivariate analysis may be projected from spectra of unknown samples, we followed the criteria proposed by Chang et al.⁴⁰ to evaluate the performance of the PLSR models: (1) RPD < 1.4, the model is not able to predict the target property; (2) 1.4 ≤ RPD < 2.0, moderate model predictive performance; (3) 2.0 ≤ RPD, the model can predict the target property well.

Following these criteria, waxes, naphthalenes volume fractions, and sulfur content could not be predicted. Indeed, for those, even if the calibration model seems good, the predictions are unsatisfactory and lead to significant errors. In contrast, the volume fractions of paraffin and aromatics, the kinematic viscosity and the API could be well estimated with predictive RPDs of 2.88, 2.66, 2.38, and 2.31, respectively, leading to average prediction errors of 10% for paraffin volume fraction, 8% for aromatic volume fraction, 16% for kinematic viscosity, and 6% for °API.

Analytical Method Validation and Testing with Real Samples. The good prediction of the crude oils' °API, kinematic viscosity, and composition parameters from the combination of a portable device, a spectral database, and a robust statistical method is of great interest for on-site testing. Indeed, crude oils with a high °API, low viscosity, and high aromatic content are considered the most toxic, can easily spread on water, and are usually flammable, their spills producing a massive environmental impact. In addition to these parameters that are important for depollution, the determination of the paraffin volume fraction of a crude oil gives valuable information for the processing of the crude oil.

To assess the capacity of the analytical tool for real-life scenarios, spectra of various samples from oil spills, weathered oils, mousse (oil/water mixture), or sediment–oil agglomerates (SOA) were analyzed. The predicted parameters from oil spill exercises included can be compared with the parameters of the crude oils that were reported to be used: Statfjord²¹ and Ekofisk crude oils.³² The estimated values for the kinematic viscosity were obtained with larger errors from 7.9 to 38.3%. The prediction of the volume fractions of aromatics and paraffins shows deviations from the reported values of 3.1 to 6.2 and 0.1 to 12.5%, respectively. Finally, the values obtained for the °API showed errors from 0.2 to 8.6% (Figure 3 and Tables S4–S5). Such predictions with reasonable errors confirm the ability of the developed analytical tool for rapid on-site parameter estimation to help in immediate and adequate action.

Similarly, the predicted parameters for simulated weathered Arabian light crude oil (100, 150, 200, and 250 °C) showed coherent trends with reported experimental observations (Figures 4 and S11). The °API and kinematic viscosity, especially, are increasing upon more intense weathering.⁴¹ Predicted volume fractions of paraffins and aromatics are both decreasing quickly during the first weathering stages, in accordance with the observed rapid evaporation or dilution of short alkanes from or in water and the oxidation to oxyhydrocarbons or the formation of PAHs.⁴²

Mixtures of crude oil from the Oseberg field (NOR) with Baltic Sea (Greifswald, DEU) water and Teltow Canal (Berlin, DEU) water were prepared by mixing for 2 h on a rotary mixer. As described in literature, the emulsions remained stable up to 70% of water.⁴³ Similarly, a sand-based sample (SOA) was

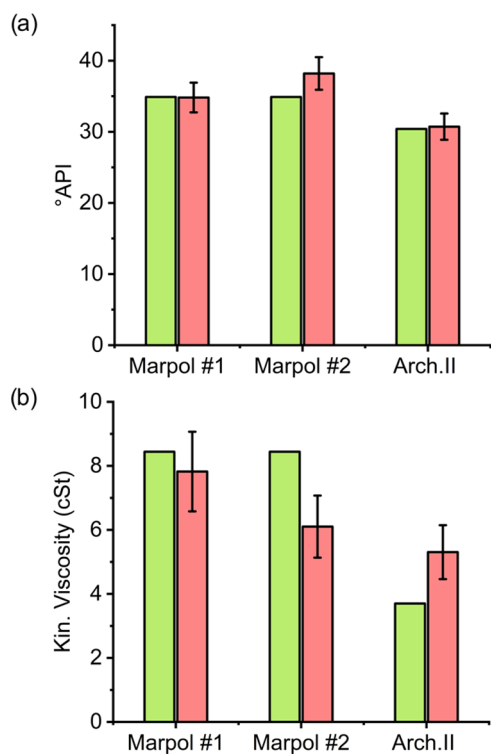


Figure 3. Predicted physical parameters for the two Marpol exercise samples from 1986 and the Archimedes 2 experiment from 1985: (a) °API and (b) kinetic viscosity (cSt).

obtained by mixing sea sand (82%), Baltic seawater (3%), and Oseberg crude oil (15%).⁴⁴ Upon analysis of those samples with the analytical tool, their parameters could be predicted (Figures 4 and S12). In the case of mousses, the emulsion density should ideally correspond to the density and proportion of both liquids. However, the results were inconclusive in this regard as the method primarily measures the aggregation or π -stacking of PAH species that predominantly remain in the oil phase. Paraffin and aromatic fractions show opposite behavior for seawater- and fresh water-based mousse or SOA, presumably because of the higher electrolyte content of seawater. Unpredictable and uneven water uptake or adsorption of organic molecules onto sand granulates could be the cause of the instability of the predicted parameters.^{45,46} Finally and importantly, a significant increase in kinematic viscosity was observed for crude oil-based mousses compared to their original crude oils, as described in previous studies.^{43,47} This phenomenon is also reflected in the predicted results for SOA, despite its predominantly agglomerate composition.

CONCLUSIONS

The development of a wireless portable prototype for spectral analyses, based on the unique emission fingerprints of crude oils, represents a significant advancement in oil spill characterization. This analytical tool, in conjunction with multivariate analysis, allows for the rapid, accurate, and cost-effective classification of crude oils. In addition to the spectra, the prototype collects physical properties such as API and kinematic viscosity, as well as composition parameters such as sulfur content, naphthalenes, waxes, and volume fractions of aromatics and paraffins, from various sources. By developing an empirical relationship between these parameters and the emission fingerprints, the prototype enables the prediction of

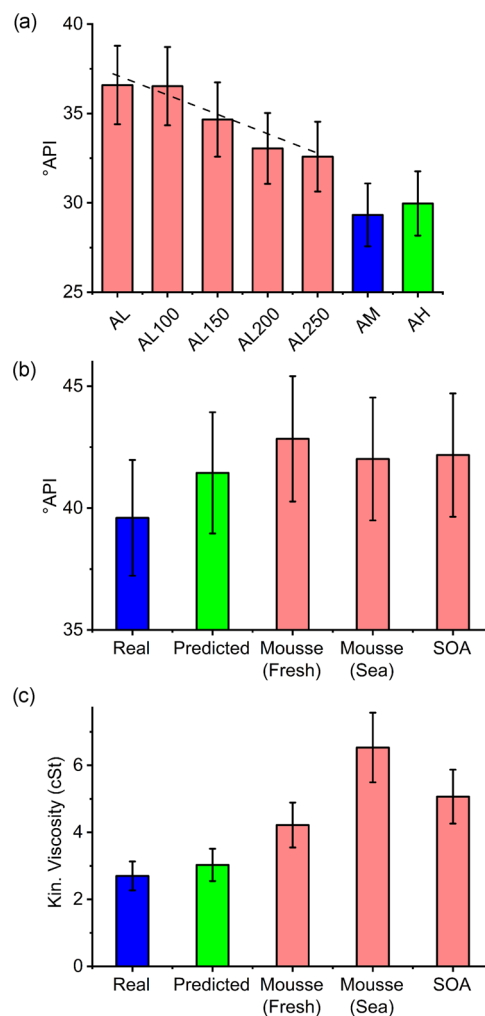


Figure 4. Predicted physical parameters for (a) Arabian light crude oil fresh (AL) or weathered at 100 °C (AL100), 150 °C (AL150), 200 °C (AL200), 250 °C (AL250), Arabian medium (AM, blue), and heavy (AH, green) crude oils. (b) and (c) Real (blue) and predicted physical parameters for Oseberg crude oil (green) and corresponding emulsion (70% water) with fresh water and seawater and sediment–oil agglomerates: (b) API degree and (c) kinetic viscosity (cSt).

key properties such as API, kinematic viscosity, and paraffin and aromatic volume fractions, with remarkable accuracy.

To validate the predictive capabilities of the prototype, spectra of oil spill exercises, oil spill experiments, water–oil emulsions, weathered samples, and sediment–oil agglomerates were analyzed. The comparison of the predicted values with crude oils of published and described behavior upon spill or weathering further confirmed the accuracy of the predictive model.

Current research is focused first on enhancing the prototype's portability by integrating the multivariate analysis algorithm directly into the microcontroller. Additionally, the development of a neuronal network-based algorithm will further enhance the robustness and accuracy of the prototype, even upon entering unknown samples into the "learning" database for instance, during a depollution campaign. Alternatively, the prototype should also be suitable for vegetable oil analyses, potentially providing a complementary alternative to existing IR methods.^{48,49} The combination of a portable reader and multivariate analysis offers a comple-

mentary approach to classical methods for oil characterization, advancing the field of on-site oil analysis.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.3c00648>.

Instrumentation; sample data; spectral database, and principal component analyses and partial least-squares regression and prediction (PDF)

Spectral database (XLSX)

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CRedit: Maria Mansurova conceptualization, investigation, writing-review & editing; Sergej Johann conceptualization, investigation, software; Harald Kohlhoff conceptualization, investigation; Knut Rurack supervision, writing-review & editing; Matthias Bartholmai supervision; Jérémy Bell conceptualization, funding acquisition, investigation, project administration, supervision, validation, writing-original draft, writing-review & editing.

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Notes

The authors declare no competing financial interest.

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