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# Sensors and Electronic Instrumentation Advances

## Proceedings

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**(018)**

# Reaction-Based Fingerprinting Methods in Natural Water Discrimination and Analysis

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**Summary:** Optical fingerprinting is a versatile and effective tool that has numerous applications in the discrimination and classification of samples. A novel approach in fingerprint methods is using reactions occurring over time instead of static data. In the current research we propose a reaction-based optical sensing method for the discrimination of unpolluted and artificially contaminated water. Waters from different sources were added to the reaction mixture containing carbocyanine dye and an oxidant in a 96-well plate. Absorbance and fluorescence of the mixture were measured photographically over time as reactions occurred. The data were processed using linear discriminant analysis. Natural water samples were distinguished from waste water samples. 11 water samples from boreholes, ponds, springs, and wells and samples of tap water were successfully discriminated; water samples artificially contaminated with a soluble fraction of engine oil (WSF) were distinguished from unpolluted samples. The feasibility of detection of 35-fold diluted WSF was shown. This innovative strategy has potential applications in water pollution monitoring.

**Keywords:** Optical sensing, Fingerprinting, Indicator reaction, Water pollution.

## 1. Introduction

Water pollution is a major environmental problem that affects not only animals and plants but people's daily lives. It is crucial to strictly monitor drinking water sources, which requires the development of precise, high-throughput, and cost-effective methods for water analysis.

Pattern recognition or fingerprinting technique is widely used for solving screening tasks. Based on chemometrics, these methods can deal with various problems, such as discrimination, clustering, identification and authentication of samples, as well as quantitation of individual components [1]. Analytes can be clearly identified by characterizing the unique response patterns.

The fingerprinting methods compare the characteristics of samples without determining the concentrations of any particular compounds. The emerging methods, that can be referred to as "reaction-based sensing", involve several measurements in the course of the reaction in contrast to the traditional colorimetric and fluorimetric fingerprinting methods, which measure the signal after the analytical reaction is complete. [2, 3] Periodic measurements of absorbance or fluorescence intensity increase the amount of information from the samples and characterize them more precisely than equilibrium-based methods.

Due to simplicity and high throughput, fingerprinting methods make it possible to test a large number of water sources in a short period of time; they can solve the tasks of detection and quantification of pollutants as well as the identification of their sources. By using kinetic data from indicator reactions, the efficiency of fingerprinting methods can be enhanced, providing a more detailed characterization of samples. Examples of the application of fingerprinting for water analysis include determining water quality parameters and odor concentration by electronic nose [4]; attributing private well contamination to a particular source [5]; identifying sources of heavy metal contamination in river sediments [6].

Previously we successfully applied the kinetic approach for discrimination of individual compounds, proteins, engine oils, and irradiation doses absorbed by food products [7-11]. The present study aimed to explore the potential of applying the reaction-based optical fingerprinting strategy for the discrimination of unpolluted water samples; another task was to recognize artificially contaminated samples. We selected engine oil as an organic model pollutant, the water-soluble components of which cause contamination.

The primary goal of this research is to evaluate the ability of the proposed approach in identifying and quantifying both types of pollutants in different water samples. The effect of both pollutants was studied using the same scheme.

## 2. Methods

Nine samples from natural water sources collected in central Russia (pond, spring, well, and borehole) and two samples of tap water, a total of eleven samples, were examined in the current work, in addition to three samples of waste water..

To artificially contaminate the water samples with engine oil, 12.5 mL of water was mixed with 100 µL of oil, shaken for 0.5 min, and placed on an orbital rotator for 24 hours. After settling the emulsion, the water phase was separated by filtering through a wetted cellulose filter. The resulting water-soluble fraction (WSF) was diluted with the corresponding water sample to create various dilutions of WSF, and a portion of the solution was used in the indicator reaction.

The general protocol includes mixing the sample and reactant solutions (dye, buffer components, and oxidant) in 96-well fluorimetric plates. Indicator reactions were carried out with carbocyanine dyes of different structures and $H_2O_2$, NaOCl, and $O_2$ as oxidants. Six replicate runs were conducted for each sample. After the start of the reaction, signals of four different types were obtained every few minutes: (1) under visible light for absorption; (2) and (3) under UV excitation (254 and 365 nm, respectively); and (4) under red LED excitation (660 nm, measurement of emission in the range of 700–800 nm). The average intensities of each well were determined using ImageJ (Fiji) software and organized into a table with columns corresponding to the intensities of spectral channels measured at different reaction times and the rows corresponding to different observations. The obtained data were processed using linear discriminant analysis (LDA) in XLSTAT, a MS Excel 2012–2016 add-on, and the data columns were considered variables. The accuracy of the model was evaluated using an automatic validation procedure. Attempts to apply other methods of data processing, such as k-nearest neighbors, Naive Bayes classifier or logistic regression, have not shown significant results.

## 3. Results

### 3.1. Discrimination of Natural Water Samples and Wastewaters

Redox reactions result in changes in color and fluorescence of carbocyanine dyes upon oxidation. Since different samples have different influence on the reaction rate, we studied a wide range of indicator reactions to select the most efficient ones. In order to use a reaction-based technique for water sample discrimination, indicator reactions were conducted in the presence of the samples.

To start with, we explored whether the proposed approach could be used to distinguish between wastewater and natural water samples. We introduced three sewage and three natural water samples into the system NaOCl – carbocyanine dye. Wastewater samples were completely discriminated by LDA from the natural waters and Millipore water, which was considered as a control sample (Fig. 1). Despite the fact that natural water samples were very similar to the control sample, there was still a small difference in the oxidation reaction rate. These samples were grouped together on the LDA score plot, but they could be distinguished with a 75% accuracy when processing without wastewater. (Fig. 2).

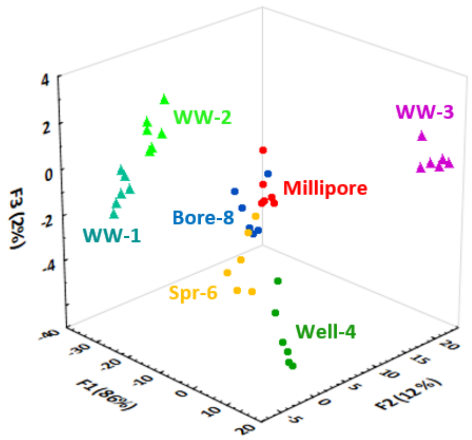


**Fig. 1.** LDA score plot for the discrimination of three natural and three wastewater samples.

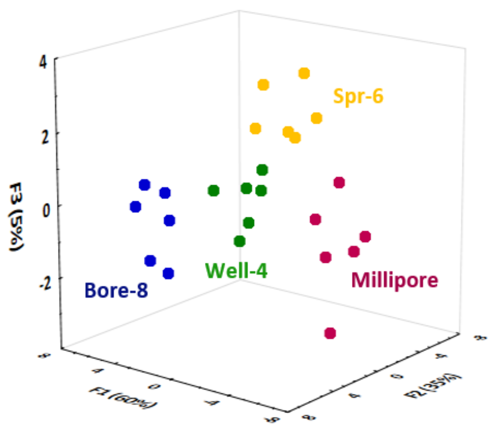


**Fig. 2.** LDA score plot for the discrimination of three natural water samples and Millipore water.

### 3.2. Discrimination of Clean Water Samples

In another experiment, we increased the amount of natural water samples up to eleven. Using the data collected during the oxidation reaction of carbocyanine dye with NaOCl, 100 % accuracy for all clean water samples was achieved. LDA score plot illustrating the discrimination of 11 water samples is shown in Fig. 3.

Identifying the clean water samples by water type was another task that was accomplished with the data obtained from the previously mentioned experiments. The data were reorganized by the types of water and processed by LDA, which made it possible to discriminate five different types of water (well, spring, tap, pond, and borehole) with 96 % accuracy with the oxidation reaction of carbocyanine dye with NaOCl.

### 3.3. Discrimination of Water Samples Polluted with Engine Oil Water-Soluble Fraction

Contamination results from the transfer of water-soluble components from engine oil, which is made up of a complex mixture of organic chemicals, when it comes into contact with water. We added engine oil to the clean water samples that were previously examined, and then we introduced the resulting WSF to the indicator reactions.

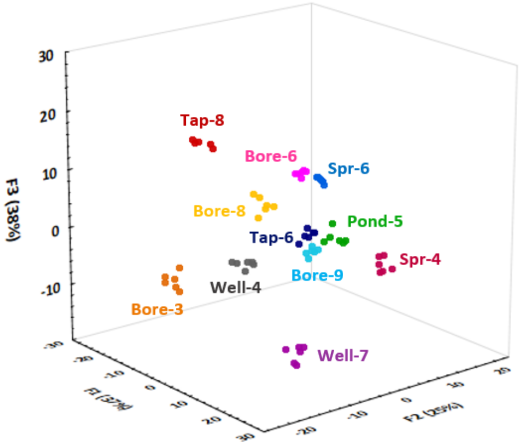


**Fig. 3.** LDA score plot for the discrimination of 11 water samples.

Oxidation reactions are able to differentiate between the clean water (of any type studied) and the WSF-containing water (of any type as well) with 100 % accuracy (two corresponding ellipses are shown on Fig. 4). Moreover, the individual water samples containing WSF are also discriminated from each other and from the unpolluted samples with accuracies of 92 % and 94 % using two indicator reactions. As a result, the water samples can be identified independently of the WSF presence, as well as WSF can be detected in different types of water.

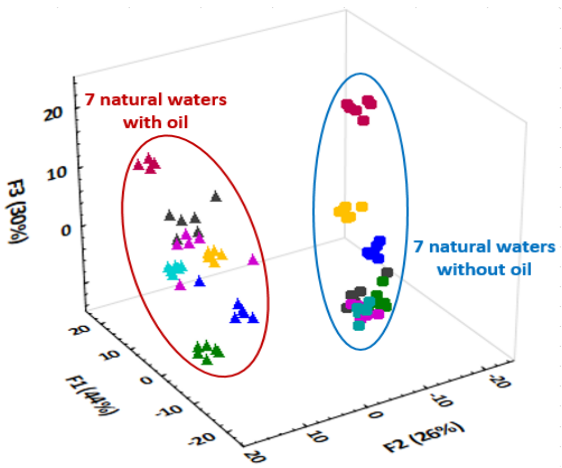


**Fig. 4.** LDA score plot for discrimination of 7 water samples with and without added water-soluble fraction of oil.

Another experiment was conducted to prove the possibility of detecting diluted WSF and to determine the maximum dilution at which it could be detected. Samples of tap and well water containing WSF were diluted with clean water of the same type in different proportions, up to 1:35, and the resulting solutions were introduced into indicator reactions. The highest dilutions studied (35 fold) were successfully distinguished from corresponding clean water and samples with lower dilutions (18-fold). The indicator reaction of oxidation of carbocyanine dye with NaOCl demonstrated a high discrimination accuracy of 92 %, indicating that it is possible to distinguish between WSF dilution degrees ranging from undiluted to 35-fold diluted (Fig. 5). Another indicator reaction of oxidation of carbocyanine dye with $H_2O_2$ showed lower accuracy (75 %), but it is still useful for qualitative evaluation. The obtained results indicate the possibility of semi-quantitative estimation of the dilution degree of the oil WSF in different types of water.

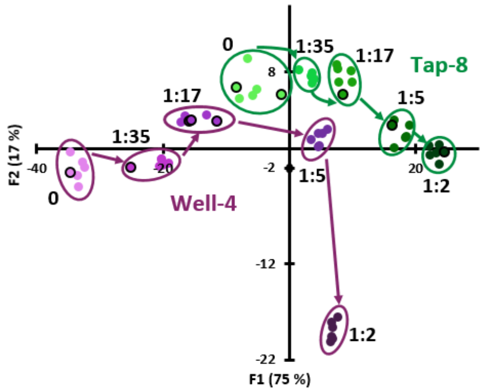


**Fig. 5.** Effect of the dilution degree of the WSF (shown beyond each confidence ellipse) on the indicator reaction.

## 4. Conclusions

Fingerprinting techniques are versatile methods that can be used to detect both unknown and expected contaminants in water. These techniques are sensitive to a wide range of compounds, making them suitable for monitoring water quality.

One application of fingerprinting techniques is the detection of unknown contaminants in water. These methods can identify substances that may be present in the water but are not typically monitored, as the method is sensitive to the overall composition of water. This can be useful for detecting unexpected pollution.

Another application of fingerprinting methods in water testing is to identify expected contaminants. In our work it was a water-soluble fraction of engine oil that can be detected even after 35-fold dilution. Moreover, the water samples can be recognized independently of the WSF presence, as well as WSF can be detected in different types of water. This demonstrates the ability of fingerprinting techniques to detect specific contaminants in water.

The advantage of fingerprinting techniques is that there is no necessity to explain the detailed mechanism that underlies discrimination. Discrimination is possible when each sample has a particular effect on the shape of the kinetic curves as a result of its individual chemical composition.

One general limitation of fingerprinting methods is the requirement to compare results from three different groups of samples: clean water, water with pollutants, and unknown samples. This comparison is necessary for accurately detecting contaminants and determining the degree of contamination. This necessity is a typical feature of fingerprinting methods, which compare samples rather than determine their absolute properties. Therefore, both clean and contaminated water must be available to obtain the correct results. Additionally, changing the reaction conditions or even choosing other reactions is essential when analyzing new contaminants. The methodology as a whole is empirical, so the search for indicator reactions is also empirical.

Overall, the proposed optical sensing technique based on indicator reactions proved to be effective in analyzing water samples. The protocol is technically simple, rapid, has a high throughput, and does not require sample preparation.

## Acknowledgements

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