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Instrumentation for the monitoring of toxic pollutants in water resources by means of neural network analysis of absorption and fluorescence spectra

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Abstract

The concentration of several pollutants, usually present in industrial waste waters, is predicted by the neural network data processing of absorption and fluorescence measurements in the visible spectral range. Proper network training provides quantitative analysis of many pollutants with sub-ppm resolution. Compact optical fibre instrumentation for absorption spectroscopy and an innovative flowcell for fluorescence measurements enable cost-effective, in situ, nonstop monitoring of waste waters.

Keywords: Pollutants; Water; Absorption spectroscopy; Fibre optics; Sensor; Fluorescence spectroscopy; Neural network analysis

1. Introduction

The demand for real-time monitoring of toxic pollutants is steadily growing as human activities increasingly pollute drinking- and seawater resources. The most-polluting substances and their maximum allowed concentrations are summarized in Table 1. In this work, we propose to optically monitor a targeted group of pollutants in situ by innovative optical instrumentation. The absorption and fluorescence measurements are processed by a novel neural network analysis scheme.

The substances identified by the authors as primary pollutants in their countries were chromium, lead, copper, sulfide, benzene, toluene, and naphthalene, alone or in mixtures. Discharges from the tanning industry are mostly to blame for the presence of chromium, lead, copper, and sulfide. Water contaminated by these pollutants has absorption spectra in the visible spectral range that are modulated by pollutant concentrations. Benzene, toluene, and naphthalene produced by the oil industry are detected by fluorescence measurements.

A neural network analysis of the measured spectra was used to predict pollutant concentration. The same data processing scheme was applied to both absorption and fluorescence spectra. Custom fibre optic instrumentation for on-line absorption spectroscopy and an original flowcell for fluorescence measurements provided nonstop water monitoring. The system has the advantage of not requiring sampling or the presence of skilled operators.

The novelty and uniqueness of this work lie in its synergetic effect, far greater than the sum of the individual contributions, which has produced not only a successful quantitative neural network analysis of measured spectra, but which has also showed the possibility of using simple, basic cost-effective concepts and instrumentation. The cumulative efforts of scientists from four different countries (Cyprus, Israel, Italy, and the UK) addressed a major need of Mediterranean countries, i.e., the monitoring of water, a resource which is becoming increasingly scarce in the Mediterranean basin. The results achieved by this synergy represent an advance in monitoring the pollutants affecting the vast majority of European countries.

After presenting the spectroscopic (Section 2) and the neural network models (Section 3), we proceed to apply them to both

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Table 1
Maximum allowed concentration of several undesirable substances in excessive amounts and toxic substances in drinking water

Aluminium	200 ppb
Arsenic	50 ppb
Cadmium	5 ppb
Chromium	50 ppb
Mercury	1 ppb
Nickel	50 ppb
Lead	50 ppb
Antimony	10 ppb
Selenium	10 ppb
Boron	2 ppm
Iron	200 ppb
Manganese	50 ppb
Copper	3 ppm
Silver	10 ppb
Zinc	5 ppm
Phosphorus	5 ppm
Fluorides	700 ppb
Calcium	250 ppm
Magnesium	50 ppm
Sodium	150 ppm
Potassium	12 ppm
Nitrogen	1 ppm
Cyanides	50 ppb
Chlorides	400 ppm
Sulfates	250 ppm
Nitrates	50 ppm
Nitrides	100 ppb
Ammonium	500 ppb
PAH	0.2 ppb
Benzo 3,4 pyrene	0.01 ppb
Tetrachloromethane	3 ppb
Trichloroethane	30 ppb
Tetrachloroethene	10 ppb

absorption (Section 4) and fluorescent data (Section 5). Section 6 presents a compact fibre optic probe for in situ absorption measurements, while Section 7 describes a simple flow cell for drawing water for fluorescent analysis.

2. Spectroscopic models

The same model is applied to both absorption and fluorescence measurements and is based upon the well-known Beer Lambert law [1]. For low pollutants concentrations we have:

$$\mathrm{OD}(\{c_i\}, \lambda) = \sum_i c_i \cdot \mathrm{OD}_i(\lambda) \tag{1}$$

$$F(\{c_i\}, \lambda) = \sum_i c_i \cdot F_i(\lambda), \tag{2}$$

where $\mathrm{OD}_i(\lambda)$ is the optical density at wavelength λ, of the ith component, whose concentration is c_i, $\mathrm{OD}(\lambda)$ the optical density of the mixture, with corresponding expressions for the fluorescence intensities $F_i(\lambda)$ and $F(\lambda)$ (normalized by the intensity of the exciting light).

Once we know the spectra of all the components $\{\mathrm{OD}_i(\lambda); F_i(\lambda)\}$ and measure the spectrum of the mixture $\{\mathrm{OD}(\{c_i\}, \lambda); F(\{c_i\}, \lambda)\}$, we can use a mathematical tool to estimate the $\{c_i\}$.

3. The neural network

Real-time estimation of pollutant concentrations requires the handling of large amounts of data in the presence of noise. Many methods have been developed to address this issue. Few of them, such as principal component regression, partial least square regression, multivariate calibration based on the linear mixture model and others are described in ref. [2]. Most of the techniques rely on some sort of least mean square regression in combination with data compression. Any least mean square algorithm basically involves a matrix inversion. As the amount of data collected increases, the matrix inversion can become non-trivial. Thus, the quest for data compression is understood.

In this work we chose to use artificial neural network data processing with a modified error function. Neural networks can be trained using laboratory calibrated measurements [3–5]. Once trained, it can be used to process experimental data to determine both the pollutant species and their relative concentration at a much faster rate than for example, non-negative least mean square estimation methods. We found that a linear perception-based neural network can provide both simplicity and sufficient performance [4].

Mathematically, if $\vec{p}$ is a column vector representing the measured spectral data and $\vec{o}$ is a column vector representing the concentrations of the various pollutants (components), then our neural network can be expressed by the following equation:

$$\vec{o} = \vec{b} + \boldsymbol{W} \cdot \vec{p}, \tag{3}$$

where $\mathbf{W}$ and $\vec{b}$ denote the network matrices of weights and bias vector, respectively. To create a network, which produces the correct output for a given input, it is necessary to adjust these weight and bias parameters. This is done in a procedure called training. Using N laboratory-made solutions of M components at known concentrations, $\vec{t}_n = \{c_1^{(n)}, \ldots, c_M^{(n)}\}^{\mathrm{T}}$ ($n = 1, \ldots, N$ and T denotes vector transpose), we found those $\mathbf{W}$ and $\vec{b}$ that best satisfy $\vec{t}_n = \vec{b} + \boldsymbol{W} \cdot \vec{p}_n$ for all $n = 1, \ldots, N$. Using the iterative error backpropagation method [3,4], we started with an arbitrary guess of $\mathbf{W}$ and $\vec{b}$, calculated $\vec{o}$ from Eq. (3), generated an error vector $\vec{e}$ from Eq. (5) below, and used the error to iteratively modify $\mathbf{W}$ and $\vec{b}$ using

$$\mathrm{d}\vec{b} = \mathrm{lr} \cdot \vec{e}; \qquad \mathrm{d}\boldsymbol{W} = \mathrm{lr} \cdot \vec{e} \cdot \vec{p}^{\mathrm{T}} \quad \text{(outer vector product)}, \tag{4}$$

until the error fell below a desired threshold. lr determines the weight and biases changing rate.

To maintain similar precision over a wide range of concentrations we chose a fractional error measure given by:

$$\vec{e} = \left\{ e_1, \ldots, e_i = 10 \log_{10}\left(\frac{t_i}{o_i}\right), \ldots, e_M \right\}^{\mathrm{T}}. \tag{5}$$

There are many methods to determine the appropriate learning rate such that the learning convergence would be fast, without oscillations and would prevent getting stuck in local minima. We used both the adaptive learning and the momentum methods [3–5].

The above mention architecture and training method for the neural network practically causes the neural network to assign