

Multichannel Spectroellipsometric Technology for Aquatic Environment Diagnostic

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Abstract A compact measuring - information multi-channel spectroellipsometric system for monitoring the quality of aquatic environment, that is based on the combined use of spectroellipsometry and training, classification, and identification algorithms is described. This system is differed from modern analogues by the use of a new and very promising method of ellipsometric measurements, an original element base of polarization optics and a complex mathematical approach to estimating the quality of a water object subjected to anthropogenic influence. The spectroellipsometric system can be used in different fields where the water quality should be estimated or the presence of a particular set of chemical elements should be revealed. The system solves these problems by real-time monitoring of the aquatic environment. In the stationary version it allows the tracking of the dynamics of water quality in a stream, and when placed on a ship, it allows the measurement of water parameters along the route. Some experimental data and calculations are given. Assessment of the system precision is realized for water reservoirs located in South Vietnam.

Keywords Water Pollution, Spectroellipsometer, Algorithm, Expert System, Identification, Spectrum

1. Introduction

Problem of the aquatic environment operative diagnostics is arisen practically in many human base including agriculture, medicine, industry and service. The development of these anthropogenic processes poses the problem of water pollution control and synthesizing monitoring system for water quality assessment in active regime.

Pollutant sources can have different structures and classes. Therefore, monitoring system is to be multi-purpose and mobile. It can be realized with the use of spectroellipsometric technology that gives possibility to have the spectrums with the sensitivity of 0.01% [1,5,4,7].

The creation of multi-channel polarization optical instrumentation and use of spectroellipsometric technology are very important for the real-time ecological control of aquatic environment. It should be mentioned that efficient solution of this multi-parametric problem greatly depends on the precision and simplicity of ellipsometric devices. A technology of combined use of spectroellipsometry and algorithms of optical spectrums identification and recognition allows the creation of a standard integral complex of instrumental, algorithmic, modular and software tools for the collection and processing of data on the aquatic environment quality with forecasting and decision - making functions [2, 3].

Some realizations of the spectroellipsometric technology were used for water quality control in South Vietnam (Cao Van Phuong *et al.*, 2009; Nguyen Xuan Man *et al.*, 2011). Pollutant sources in Vietnam were grouped in classes: agriculture sewage; domestic, municipal, and industrial waste; shipping; aquaculture; and coastal mining. The expert system for ecological control was developed as part of an agreement between the Russian Academy of Sciences and the Vietnamese Academy of Sciences and Technology to collaborate on ecoinformatics and remote sensing. Specific attention was given for the water quality control in the estuary zones taking into consideration of pollution sources compounded in territories bordering the South China Sea.

This paper describes new version of spectroellipsometric system that develops and realizes the functions of contaminant identification for multi-component solutions. It is realized by means of combined use of cluster analysis and algorithms for inverse task solution.

In this paper, we propose a new method ellipsometric measurements - ellipsometry with a binary modulation of the polarization state (BMPS) in which the sample is to alternately directed radiation with two polarization states and analyzes the signal at the photodetector . In developed ellipsometry devices BMPS with no moving polarization elements combined with high sensitivity, stability and measurement speed . This approach to solving the problem in the foreign studies spectroellipsometry not known.

2. Spectroellipsometric Expert System for the Aquatic Environment Control

Spectroellipsometric expert system for the aquatic environment diagnostics (SESAED) consists of measuring subsystem (Fig. 1) and software. The system's structure includes a compact multi-channel spectroellipsometer (MCS), information interface with computer (IIC), software (STW), and extending database (EDB). The STW realizes a number of algorithms to process data fluxes from the MCS and provides the service functions of visualization and control of measurements. The EDB consists of sets of standard spectral images of aquatic environments represented by points in the multi-dimensional vector space of indicators, pre-calculated on the basis of learning samples.

The principle behind the SESAED is based on fixing changes in light flux the MCS and digitizing them in IIC. Further processing of these data to make them more efficient

is determined by STW with algorithms capable of recognizing spectral images. The degree of adaptability of the recognition procedure is determined by the level of accumulated knowledge about intensity fluctuations and the polarizing properties of light reflected from the water surface or dispersed and refracted within the water environment. The STW enables, in case of uncertain identification of spectral images, to make an expert decision based on the visual analysis of a spectral image. This procedure is realized in dialog mode with the SESAED and, if a decision is made, the operator can fix it in the database in the form of a standard for subsequent appearances of similar spectral images.

The principal structure of the STW unit providing the identification procedure involves series algorithms (Table 1). The light intensity I_j recorded at time t_i in the channel λ_j forms two spectra that correspond to different light polarizations. Operator takes decision what algorithm will be used for identification task solution.

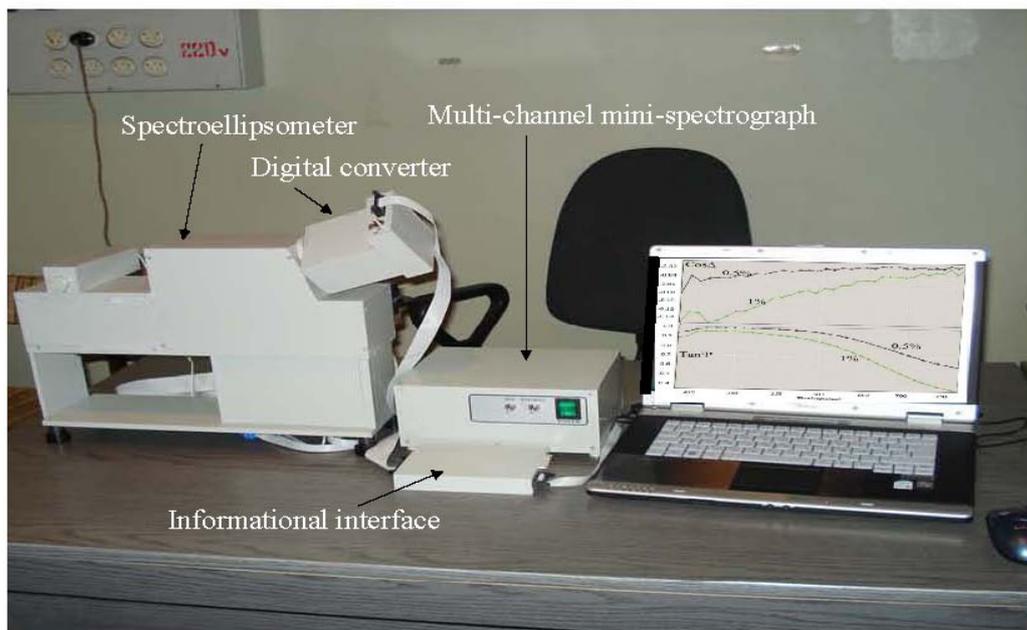


Figure 1. General view of the spectroellipsometric system.

Table 1. Description of the SESAED units

Unit	Characteristic of the unit
VOD	Visualization of observed data (spectra, correlations, statistical parameters, empirical and theoretical functions of distribution)
CPCP	Calculation of parameters for the classical procedure of decision making when using the Neuman-Pearson criterion
CSP	Calculation of statistical parameters and other characteristics, formation of the vector space $\{u_i\}$
EPPW	Estimation of parameters for the Wald sequential analysis in decision making
REDF	Reconstruction of empirical distribution functions
RFUI	Reconstruction of the functions of a user's interface equipped with software to intervene in the working regime of an expert system at any stage
RSC	Realization of statistical criterion to estimate the theoretical function of distribution
VP	Visualization procedures

After the learning procedure, the expert system is limited only by the volume of measurements fixed by the operator and proceeds from statistical reliability and the real-time regime. The operator has two possibilities to regulate this regime: establishing the volume of the series $\{\xi_j^i\}$ or fixing the time of their accumulation.

Usually the latter characteristic is chosen equal to one second. The operator is combined with SESAED units by means of the man/machine interface IIC, which provides selective control of operations in all units.

In the event of an oil slick on the water surface the system analyzes its thickness, age, source and geometry. The most informative measurements here are those made at 398 nm, 439 nm and 480 nm wavelengths. In the case of dissolved or suspended components in the water the system estimates their concentration and, from data in EDB on the hydrodynamic parameters of the water body, it calculates their spatial distribution using the methods that process two-dimensional images.

3. Data Processing Algorithms

Spectroellipsometric measurements deliver spectrums that are considered as spectral images of water solutions. Space of spectral images is formed during the learning procedure realized in laboratory conditions when spectral images and chemical analysis are performed at the same time. Identification procedure to recognize spectral image of water solution is carried out with the use of the EDB where spectrums and their derivatives are storage during learning procedure. Standard of the EDB item is given in Table 2.

An identification of spectral image of unknown water solution is realized by means of comparison his vector – identifier with elements of the EDB. Depending from used optical device spectral image of water solution can be represented by one or two vector-identifiers calculated with the use of rule described in Table 2. Final identification is realized by means of search in the EDB of vector – identifiers which are minimal distance from considered vector-identifier $Q = \{X_1, \dots, X_n\}$ of given water solution. Distance between vector-identifiers is calculated with the use of the following formula:

$$\delta = \min_n \rho(Q - Q_n) = \frac{1}{2n} \min_i \left[\sum_{j=1}^n |X_j - A_j^i| + \sqrt{\sum_{j=1}^n (X_j - A_j^i)^2} \right] \quad (1)$$

Table 2. Structure of standard spectral image of water solution. Notation: A_1 is the square occupied by spectral curve, A_2 is the maximal value of spectral curve, A_3 is the minimal value of spectral curve, A_4 is the distance between wavelengths with minimal and maximal values of spectral curve, respectively; A_5 is the maximal derivative of spectral curve; A_6 is the maximal value of second derivative of spectral curve; A_7 is the number of spectral curve maximums; A_8 is the average value of spectral curve; A_9 is the wavelength correspond to average value of spectral curve; B is the chemical element concentration.

Etalon number	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	B
1	A_{11}	A_{21}	A_{31}	A_{41}	A_{51}	A_{61}	A_{71}	A_{81}	A_{91}	B_1
.....										
n	A_{1n}	A_{2n}	A_{3n}	A_{4n}	A_{5n}	A_{6n}	A_{7n}	A_{8n}	A_{9n}	B_n

Use of (1) gives better result in comparison with the application of other known criteria of closeness between spectral curves. That is why in this case there is minimal risk to miss the situation with dangerous pollution of water reservoir. In common case, usually the following methods are used:

- *Cluster analysis.* In this case two types of clusters are formed for $\text{Cos}\Delta$ and $\text{Tan}\Psi$ where Δ and Ψ are ellipsometric angles corresponding to complex amplitude reflection coefficients for two different polarizations. Decision is made by weighted values (1) or independently for each polarization.
- *Algorithm of discrepancy between spectra.* It is assessed average distance between the ordinates for both spectra and spectrum of studied case and decision is made taking into account minimal value of this distance.
- *Algorithm of discrepancy between etalon vectors.* In this case, decision is made taking into consideration of minimal δ .
- *Inverse task solution.* This algorithm is based on linear dependence of optical spectrum on the concentration of chemical elements in water solution. In this case, sub-definite system of linear algebraic equations is solved.

Last algorithm allows the obtainment of concentrations for chemical elements $\{y_s, s=1, \dots, k\}$ in aquatic environment. Its meaning is in the following procedure. As a result of the MCS functioning, at moment t_i at the output of each channel λ_j ($j=1, \dots, n$) values Z_{ijp} ($i=1, \dots, m; p=1, 2$) are fixed, so that $Z_{ij1} = \text{Cos}\Delta_j + \xi_{ij}$ and $Z_{ij2} = \text{Tan}\Psi_j + \zeta_{ij}$, where Δ_j and Ψ_j spectroellipsometric polarization angles, and ξ_{ij} and ζ_{ij} are a random values (noises) with zero mean and dispersion σ_j^2 .

It is supposed that concentration of chemical elements linearly forms each spectrum:

$$\sum_{s=1}^k a_{js} y_s = Z_j^1 \quad \text{and} \quad \sum_{s=1}^k b_{js} y_s = Z_j^2, \quad (2)$$

where $Z_j^p = \frac{1}{M} \sum_{i=1}^M Z_{ijp}$ ($p=1, 2$), M is number of spectrums averaged, empirical coefficients a and b are determined when studied aquatic environment has known parameters $\{y_s, s=1, \dots, k\}$.

Practically $s < n$. In this case equations (2) are undetermined and their solution can be realized with the use of many methods. In [4] proposed analytical method based on solution dispersion minimization. This method is realized in the STW item.

4. Empirical Results

The SESAED was used in different laboratory and in-situ conditions. Table 3 shows example of vector-identifiers calculated for CuSO_4 10% solution with use of Table 2 procedure. Table 4 gives experimental results which give possibility to compare above mention algorithms. Dependence of risk assessment as function of solution concentration is represented in Fig. 2. As it follows from these results risk to have high error under the solution identification is reduced when algorithm of Table 2 is used. We see that risk to have high error is growth with increase of chemical element concentration. It is caused that discrepancy between spectra is decreased with increase of chemicals concentration. In this case it is necessary to extend the database of spectral etalons.

The SESAED was used for in-situ experiments in South Vietnam [1,6]. Fig. 3 represents normalized spectral characteristics of studied water objects. It is seen that all spectral curves I/I_0 related to water quality intersect in the point (510,0.3). This means that channel of 510 nm is invariant for studied reservoirs. As well it is followed that channels 570-690 are the most informative. Spectral images of pollution slicks for salt and oil on water surface are distinguished what gives possibility to recognize them with high reliability.

The SESAED was used for water quality control in Nuok Ngot Lagoon near Hung Lac (Vietnam) - $14^\circ 9' 0''\text{N}$; $109^\circ 10' 59.99''\text{E}$, Saigon River in Hochiminh City area, and fish-farm reservoirs in Ba Ria Province. Lagoon area was divided by ten sections location of which was uniformly distributed from the north to south. One measurement by means of the SESAED was performed in each of these locations and water sample was taken at the same time. Location 1 had coordinates $14^\circ 10'\text{N}$, $109^\circ 10'\text{E}$. Location 10 corresponded to the lagoon mouth. Table 5 allows assessment of the SESAED precision. It is supposed that water samples were assessed with very high precision.

Table 3. An example of the SESAEC database element.

Solution	Q	Vector-identifiers								
CuSO_4 (10%)	Q_A	21.6	0.17	0.1	143	0.67	0.12	2	0.16	0.21
	Q_ψ	43.1	0.89	0.04	201	0.59	0.09	3	0.65	0.01

Table 4. Comparatively assessment of algorithms for recognition of spectral images of water solutions.

Object for study	Identification algorithm and its error (%)			
	Cluster analysis	Discrepancy between spectra	Discrepancy between vector-etalons with the use equation (1)	Inverse task solution
CuSO_4	15	12	8	7
NaCl	17	11	7	5
NaHCO_3	16	10	5	5
NH_4OH	21	13	9	6
ZnSO_4	22	12	8	6
Potassium iodite	13	10	6	4
Na+Cu+Zn+Mn+glucose	18	9	9	8
Furaciline	23	11	5	5
Bifidumbacterium	14	10	4	4

Table 5. Comparison of data received by means of the SESAED and *in situ* measurements in Nuok Ngot Lagoon.

Location	Water salinity (‰)		Turbidity (mg/l)		pH		PO_4^{-3} (mg/l)	
	SESAED	On-site	SESAED	On-site	SESAED	On-site	SESAED	On-site
1	30.15	33.5	12.40	10	7.04	7.82	0.033	0.03
2	23.14	26.0	24.78	21	7.71	7.79	0.034	0.03
3	26.48	29.1	29.70	27	7.66	7.58	0.068	0.45
4	27.37	32.2	26.88	24	8.01	7.78	0.023	0.02
5	28.53	31.7	45.59	47	7.29	7.84	0.042	0.04
6	28.40	26.3	29.97	27	7.22	7.52	0.082	0.10
7	27.50	25.7	23.94	21	7.45	7.30	0.067	0.35
8	26.16	25.4	34.58	38	7.21	7.75	0.023	0.02
9	26.54	30.5	48.45	51	7.09	7.71	0.023	0.02
10	20.95	26.5	60.48	63	7.63	7.00	0.039	0.05
Average error, %	10.7		11.0		6.0		27.4	

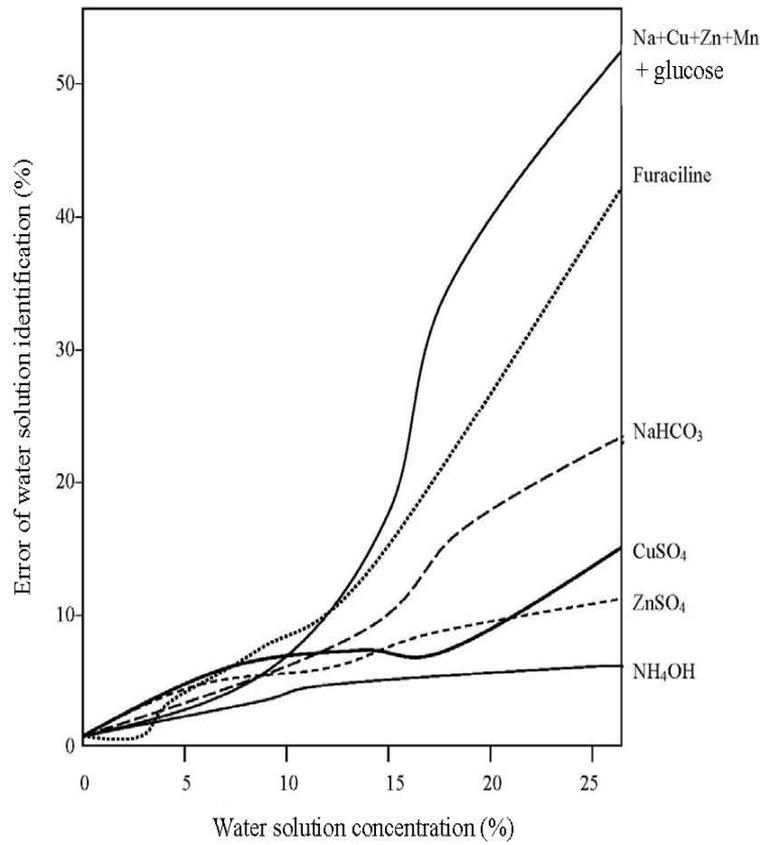


Figure 2. Dependence of spectral image identification on the solution concentration.

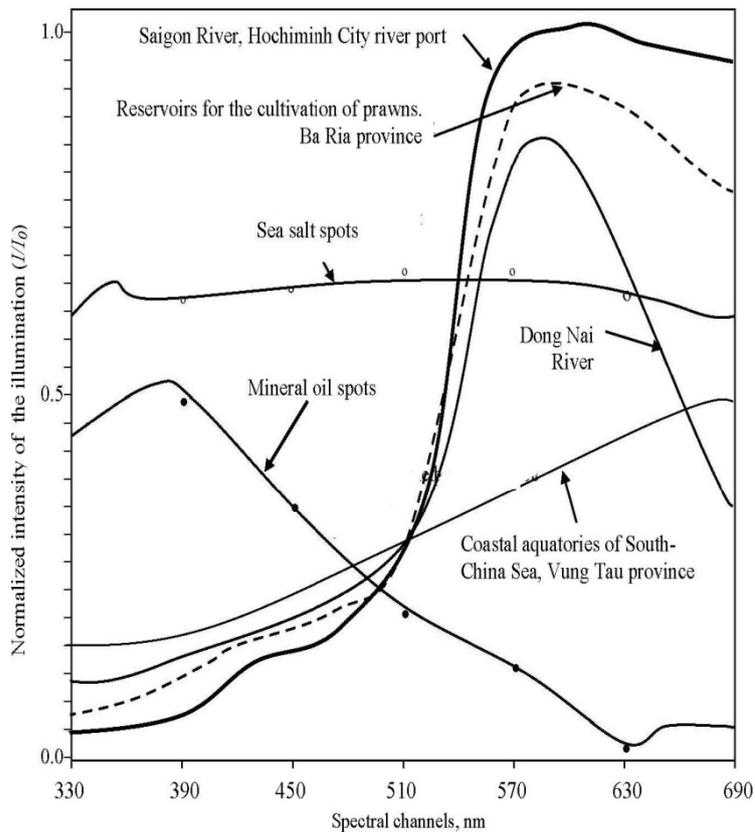


Figure 3. Spectral characteristics of some reservoirs located in South Vietnam. Notation: I is registered illumination, I_0 is light intensity of free air

5. Conclusion

The main objective of work is to create in future the compact information systems for monitoring the quality of aquatic environment and to investigate their potential efficiency. These systems are based on the combined application of spectroellipsometry methods and algorithms of training, classification, and identification. The realization of this objective will require the combined use of engineering and algorithmic tools providing real - time measurements and data processing. The technology of combined use of spectroellipsometry and algorithms of detection and classification will allow the creation of an original system of instrumental, algorithmic, modular and software tools for the collection and processing of data on the aquatic environment with forecasting and decision-making functions. The theoretical part of the work will include the use of methods of polarization optics, mathematical statistics, the theory of pattern recognition and mathematical modeling.

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