FIBER OPTIC SYSTEM FOR WATER SPECTROSCOPY

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Abstract: An innovative series of optical fiber sensors for water monitoring, based on spectroscopic interrogation, is presented. Two types of custom-design instrumentation were developed, both making use of LED light sources and low-cost detectors to perform broadband spectral measurements in the visible spectral range. The first was designed especially to perform direct absorption spectroscopy, while the second provided turbidity measurements. Designed for water analysis and industrial process control, the proposed instruments can be used by operators with little or no technical skills.

Key words: optical fiber sensors; spectroscopy; colorimetry; online monitoring; turbidity

1. INTRODUCTION

To be able to run cost effectively, plants and processes require online monitoring by components designed to optimize operating efficiency. Optical fiber sensors, capable of performing in adverse environments, tight and/or hard-to-access spaces, and/or under real-time constraints, are increasingly replacing conventional electronic-based sensors that are not always capable of doing the job. Since they can be easily interfaced with optical data communication and secure data transmission systems, optical fiber sensors are being increasing used in industrial, automotive, avionic, military, geophysical, environmental, and biomedical applications (Culshaw and Dakin, 1988, 1989, 1996; Dakin and Culshaw, 1997; Davis et al., 1986; Grattan and Meggit, 1995, 1999a, 1999b; Krohn, 2000; Lòpez-Higuera, 2002). In addition to steadily rising quality and increasingly competitive costs, they have other welcome advantages:

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- They operate without electricity, which makes them explosion-proof and intrinsically immune to any kind of electromagnetic interference. This is a notable advantage considering the widespread use of radiating instruments.
- They are compact, lightweight, and flexible, thereby enabling them to reach what were previously inaccessible areas.
- They can withstand chemically aggressive and ionizing environments.

Spectroscopy in the visible and near infrared spectral regions is one of the most popular methods in conventional analytical chemistry (Mellon, 1950; Bauman, 1962) The intrinsic optical and mechanical characteristics of optical fibers, together with the wide availability of bright LEDs and miniaturized spectrometers, further enhance the application areas of spectroscopy, and make it possible the implementation of compact instrumentation dedicated to the monitoring of specific parameters.

This paper presents an innovative series of optical fiber sensors for water monitoring, based on spectroscopic interrogation.

- *Fiber optic systems for colorimetry*: they consist of PC-interfaced spectrophotometric units and custom software designed to fit individual sensor interrogation schemes. Their advantages include a high degree of miniaturization and compactness, flexibility, and suitability to a broad range of applications, including online water color monitoring in a water recycling plant and sea-water monitoring at the Elba Island.
- *Fiber optic systems for scattered colorimetry*: they perform multi-wavelength and multi-angle absorption spectroscopy in the visible spectral range, and made use of multivariate analysis for processing the spectral data. When similar liquids were measured, a 2D map was created. The map was populated with points, each of which represented the liquid sample with its individual and global characteristics of turbidity and also of color. Similar liquids could be mapped as clusters and, consequently, correctly assigned according to class. A successful application of scattered colorimetry was the discrimination between very similar types of water-suspended sediments.

2. FIBER OPTIC SYSTEMS FOR COLORIMETRY

The fiber optic instrumentation designed for addressing absorption spectroscopy sensors complies with the following requirements:

- High degree of compactness, i.e., the optoelectronic module plus its sources, detectors, and coupling optics fit into a compact box without requiring mechanical alignments of the optical components.

- Probe using a single optical fiber configuration, rather than bundle.
- A flexible software interface friendly enough to be used by operators with little technical background.
- Low cost optoelectronic components.

The prototype of the miniaturized fiber optic spectrophotometer for measuring the absorption spectra of liquids online is comprised of three main components:

- An optoelectronic module containing the LED sources, the spectrometer detector, and the electronic power supply.
- Custom-design fiber optic probes that allow absorption measurements of liquid samples with an optical path-length between 10 and 50 mm.
- A portable computer with custom software created in Labview® to allow dialog with the optoelectronic module and to semiautomatically acquire and store data.

Among the prototype's innovative features are compactness, cost efficiency, adaptability to specified application, ability to carry out semiautomatic and automatic measurements even under the supervision of inexperienced personnel, and low maintenance costs.

The optoelectronic module makes use of a set of LEDs to obtain a low-cost source, and a fiber optic microspectrometer by STEAG-Microparts as the detector (Boehringer Ingelheim microParts, 2005). The measuring range is from 380 to 780 nm, with 10 nm resolution, and a long-term stability of 2%. A six-LED source is provided, affording a uniform spectral intensity. The LEDs are temperature-controlled by Peltier cells to optimize source stability in terms of spectral shape and intensity. The source is made of three LEDs with broadband white emissions and three with emission peaks at 420, 500, and 640 nm. The LEDs are housed in ST-compatible receptacles for easy fiber coupling; the fiber bundle from LEDs is connected to the end in a patent-pending microoptics joint allowing connection to a single optical fiber. The highest illumination efficiency is provided by a 600 μm-core optical fiber.

LabView® software, programmed to perform automatic or semiautomatic measurements and data processing, is used for optoelectronic module management. Software management of the module enhances the instrumentation's flexibility, since several programs have been written to fit different measurement requirements (Mignani and Mencaglia, 2002; Mencaglia and Mignani, 2003).

The spectrophotometer prototype and a detail of the probe for absorption measurements of liquid samples are shown in Figures 1 and 2, respectively.

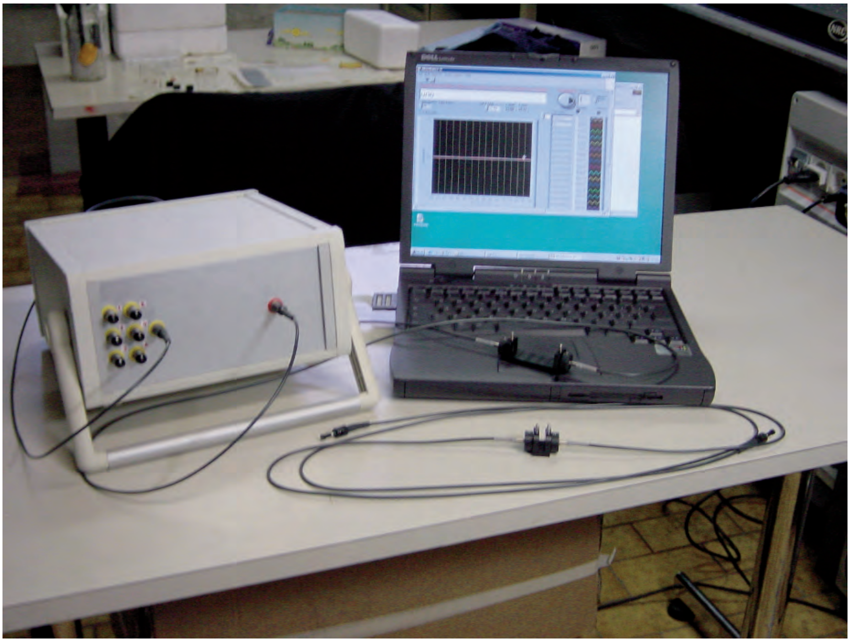

Figure 1. The prototype of the fiber optic spectrophotometer and the probes for online absorption measurements.

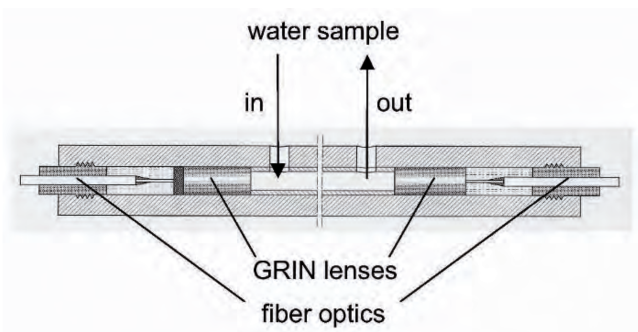

Figure 2. The fiber optic probe for measuring the absorption of liquid samples.

The prototype spectrophotometer was used in water measurements at the CONSER-IDRA water recycling plant (Prato, Italy) during October 2003. Samples (labeled A, B, and C) from three different zones were monitored (Table 1).

Table 1. The locations of the three samples analyzed from the CONSER-IDRA water recycling plant (Prato, Italy).

Sample	Location
A	Primary treatment discharge
B	Ozone treatment and recycle inlet
C	Output-recycled water

The samples were taken and analyzed over several days and at different times in order to show the absorption spectra at diverse plant operating conditions. To show the feasibility of the online measuring system, measurements were made in the recycled water inlet reservoir by placing the fiber optic probe directly inside the tank.

A set of absorption measurements are shown in Figure 3. They show that the spectrophotometer was able to follow the evolution of the samples' absorption spectra. The absorption spectra were characterized mainly by the presence of the suspended particles, which shows the same kind of scattering spectra. Nevertheless, in the case of an area of color indicating contamination, the spectra would indicate the contamination by displaying the absorption bandwidth in the vicinity of the colored area.

In addition to the absorption spectra, it is also worthwhile to calculate the integrals of the spectra that take into account the cumulative contribution of the sample color and the presence of the suspended particles, as illustrated in Figure 4. The fact that the recycled water (sample C) is of virtually constant color regardless of inlet conditions is proof that the plant is operating properly.

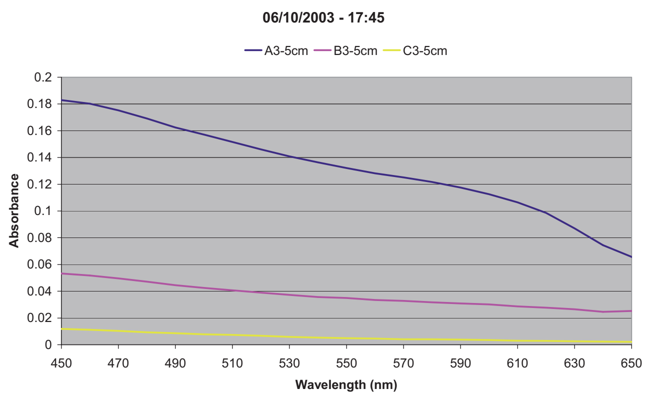

Figure 3. Absorption spectra of water samples taken from different places in the plant.

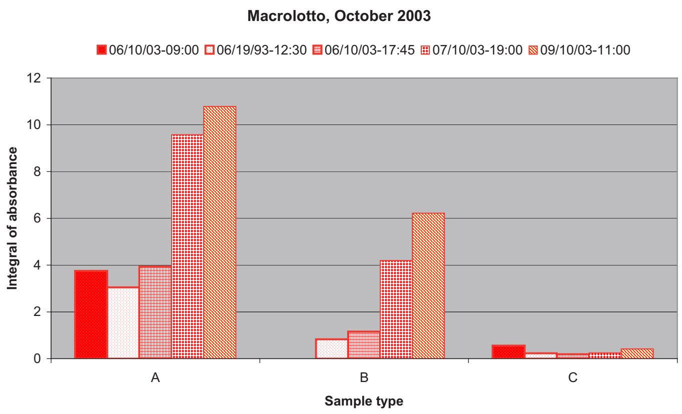

Figure 4. Integrals of the absorption spectra for the verification of the correctness of the water recycling process.

The prototype spectrophotometer was also used for sea water measurements at the Italian Elba Island to check water color at different locations and at different depths. Some spectra taken at the locations of Picco Giallo, Punta Madonna and at the harbour of Marciana Marina are shown in Figure 5. These spectra were processed by means of the Principal Component Analysis (PCA) to better cluster their similarities or differences (Cove and McNicol, 1985). The results of PCA processing are shown in Figure 6, in which the measurements result clustered according to the different locations, and also the different depths can be identified.

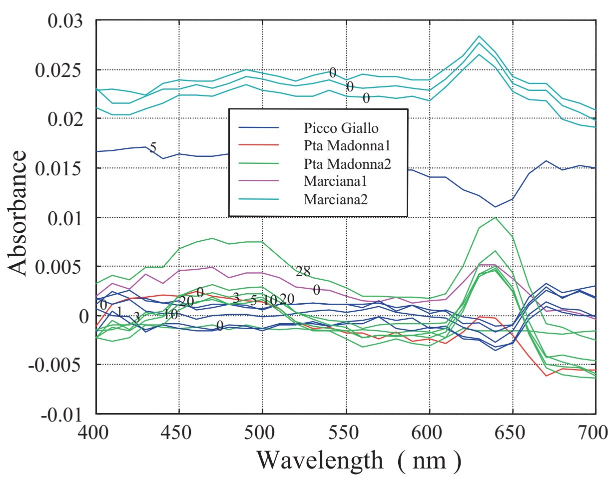

Figure 5. Absorption spectra of sea water taken at the Italian Elba Island, at different locations and depths.

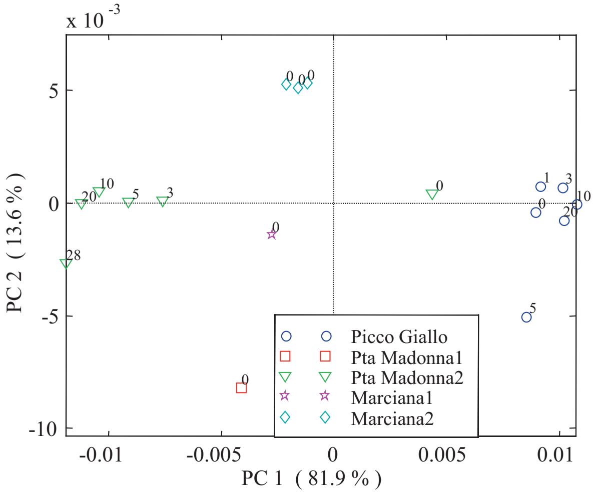

Figure 6. PCA processing of the absorption spectra capable of clustering the sea water color according to locations and depths.

3. FIBER OPTIC SYSTEMS FOR SCATTERED COLORIMETRY

Solid concentration in liquids and gases is determined by using standardised methods based on filtration and centrifuging which require the separation, drying and weighing of solids fractions. These laboratory methods are cumbersome, because they can take hours to perform and are practically impossible to automate.

In contrast, turbidity, which is an optical phenomenon due to the scattering of light by the solid particles of the suspension, is well suited for on-line and *in situ* measurements. At present, turbidity measurements are made by following the ISO7027 standard (ISO, 1984). This involves a calibrated version of the ratio between scattered and transmitted light. The ratio between the light scattered at 90 degrees and the transmitted light is measured for a formazine suspension of well-known turbidity, thus calibrating the instrument. The same quantity is then measured for an unknown suspension and is compared with that of formazine.

Although fast and practical, this method has two flaws. The first is its intrinsic ambiguity. The amount of light scattered by a suspension depends on both concentration and particle size distributions. Consequently, different concentrations of different suspensions can give the same turbidity value.

This means that it is impossible to pass from turbidity to concentration without having information on particle size distribution. Moreover, particles size itself is important information for some applications such as the testing of filter efficiency.

All this means that the turbidity standard solution must have a well-reproducible particle size distribution. This is the reason why formazine is preferred to other standards. However, formazine is the second flaw of turbidimetry, because its preparation requires the use of hydrazine sulfate, a toxic material which can be carcinogenic. Therefore, its manipulation is very dangerous. Moreover, formazine is not commercially available, and must be prepared by means of a chemical reaction, thus requiring a well-equipped laboratory (SIGRIST, 2005).

These drawbacks lead to a great demand for a new instrument that is capable of performing online turbidity monitoring and also able to discriminate among different particulates. The novel instrument presented in this paper responds to this demand. It consists of an optical fiber device that performs multi-wavelength and multi-angle scattering measurements, that is scattered colorimetry. The output is processed by means of the PCA method. This instrument has been tested by analyzing two different liquid-suspended particulates at various concentrations, thus demonstrating capability of particulate discrimination.

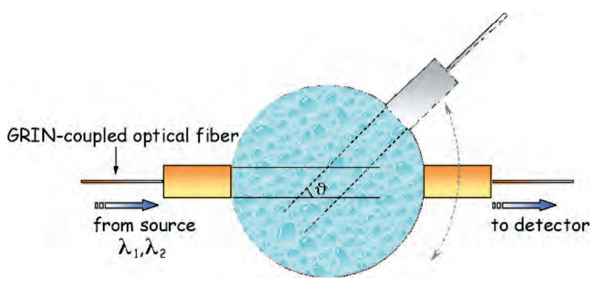

Figure 7. Working principle of scattered colorimetry.

As sketched in Figure 7, the fiber optic system for scattered colorimetry consists of a ring surrounding the test sample, along which two identical GRIN-coupled optical fibers are positioned. Fibers are connected to a light source and to a detector. The optical fiber connected to the source provides a nearly-collimated light beam. The other optical fiber, which is connected to the detector, can rotate along the ring and identifies a detecting view. A PC-interfaced rotating stage is used for motion control within a given angular range. The angle identified by the GRIN axes is the scattering angle, while the intersection between the illuminating beam and the detecting view is the area of sensitivity for multi-angular scattering measurements. The sensor output is the intensity of scattered light as a function of the scattering angle. It makes use of:

- Optical fibers 200-μm core. These fibers have large core diameter, thus enabling an efficient light coupling and the availability of high light intensity.
- NSG fiber-to-GRIN assemblies, model FCM-00F-200-0.63. These assemblies were housed in receptacles so as to avoid damage when the nephelometer was immersed in water. A glass window was placed in front of all GRINs. Silicone sealing was provided to prevent any water contact with the components inside the receptacles. The distance between the GRINs was 15 mm.
- A Micro Controle rotating stage which moves the fiber-GRIN component coupled to the detector.
- A Micro Controle TL 78 power unit and IP 28 control unit driving the stage.
- An illumination unit consisting of two commercially-available LEDs with emission in the red and IR spectral ranges and peaks at 650 nm and 850 nm, respectively. The LEDs were housed in receptacles coupled to the optical fiber by means of SMA connectors.
- A custom solid-state detector and lock-in amplifier.

This fiber optic instrument was validated by means of monodisperse LATEX beads, and demonstrated that it is able to fit the theoretical scattering patterns given by the Mie theory (Mignani et al., 2001).

The ability of the fiber optic instrument for scattered colorimetry to discriminate among different water-suspended particulates and to measure their concentration was tested by using two kinds of dust. These were obtained by filtering the basic *Arizona Fine Test Dust* (ISO12103), which is a standard material for filter testing. They are named Fine (F) and Coarse (C), and consist of particles widely polydisperse and with overlapping size distribution. Figure 8 shows the Probability Density Function of these particulates (ISO, 1997).

Scattering measurements of F and C particulates, at 650 and 850 nm, respectively were taken. Each suspension was measured at five concentrations in the 10-60 mg/L range. All scattering measurements were normalized to light intensity transmitted at 0°.

PCA was used to process the scattering/spectral data, in order to create a 2D map that clusters the different types of suspensions, thus providing their discrimination, as shown in Figure 9. The sign of the second principal component indicates the type of particulate, since the F and C particulates are identified by means of a negative or positive sign, respectively. The reliability of this map as far as particle characterization is concerned is also shown by the trend of the behavior of the principal components, which increase with concentration, converging towards zero for null concentration.

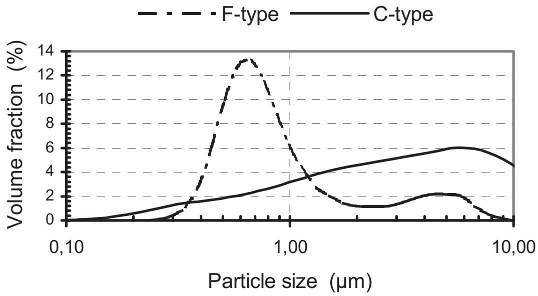

Figure 8. Probability Density Functions of F- and C-type Arizona Test Dust.

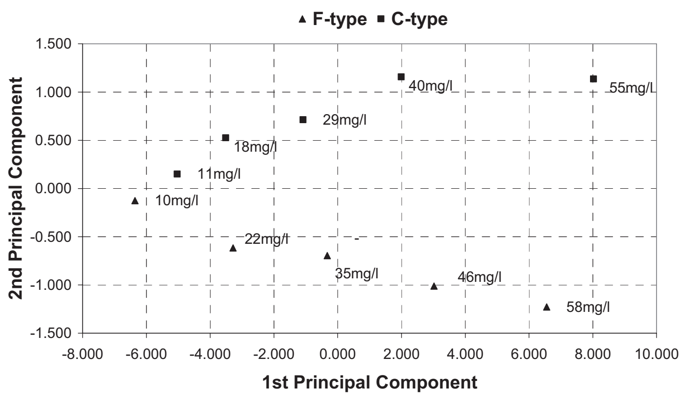

Figure 9. Discrimination of F and C particulates by means of the PCA method for scattering/spectral data processing.

4. CONCLUSIONS

The fiber optic spectrophotometers here presented comprise PC-interfaced electrooptic units programmed to fit individual sensor interrogation schemes. Their advantages include a high degree of miniaturization and compactness, flexibility, and suitability to a broad range of applications. Thanks to the availability of several functional materials for selective molecular recognition that exhibit optical absorption in the visible spectral range modulated by interaction with the analyte, the instrumentation is potentially suitable for a wide range of sensors and for olfactory perception in process control, safety, and environmental applications. Designed for the color analysis of liquids and surfaces in industrial process control, water analysis, and food processing control, the proposed spectrophotometers can be used in other colorimetric applications by operators with little or no technical skills. The presence of colorimetric passive samplers acting as dosimeters for gaseous pollutants and acids enables the instrumentation to act as an in-situ spectrophotometric laboratory, i.e. a totally autonomous nonstop monitor of passive samplers in a host of industrial and environmental applications.

The fiber optic instrument for scattered colorimetry, as it is able to provide multi-wavelength and multi-angular scattering measurements, demonstrated an ability to measure simultaneously the concentration of a suspension and its type, whether F or C, thus removing the intrinsic ambiguity of conventional turbidimeters. The use of optical fiber technology made it possible not only to obtain a compact and versatile device for online monitoring, but also an instrument capable of performing very accurate scattering measurements as far as the angular resolution of these measurements is concerned. The effectiveness of PCA data processing was enhanced by this optimized accuracy, which enabled discrimination between very similar types of particulates. For these reasons, scattered colorimetry has the potential to discriminate also mixtures of suspensions.

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