

Cr (III) and Cr (VI) detection in water environment using an optical fiber grating sensor

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ABSTRACT

This work shows the application of an optical sensor to detect the presence of Cr (III) and Cr (VI) oxidation states in water solutions. The sensing device is a long period grating produced in a standard telecommunication optical fiber by applying a suitable number of point-to-point electrical arc discharges from a fusion splicer. In order to analyze the Cr (III) and Cr (VI) solutions, the sensing device is kept into a recipient under constant longitudinal stress and the Chromium solution samples are added to it. The results show that the sensor can not only detect the presence, but also differentiate between the two-oxidation states. Samples with Chromium concentrations from 0.16 mg/l to 5.2 mg/l are analyzed, leading to maximum wavelength shifts (relative to the LPG in pure water) of 0.14 nm and 0.26 nm for Cr (III) and Cr (VI), respectively. A comparison between the results obtained for both solutions shows that is possible to identify any of the Chromium oxidation states present in the sample until a lower limit concentration of 2.6 mg/l for the employed set-up.

Keywords: Optical sensor, Chromium detection, Concentration measurement, Environment preservation

1. INTRODUCTION

Along the last years, a great number of researchers developed many works concerning to the use of fiber gratings in the measurement of physical parameters (e.g. temperature, mechanical stress and refractive index). In spite of the fact that fiber Bragg gratings (FBG) can be applied in refractive index measurements, the long period grating (LPG) has taken great attention as it presents a better sensibility to this parameter. This characteristic makes possible the use of LPG sensor in petroleum and gas fields¹ and environment control².

The LPG is a periodic modulation in the fiber core refractive index with long spatial periods (50-700 μm), which couples light from the fundamental core propagation mode to co-propagating cladding modes. This mode coupling results in attenuation dips in the fiber transmission spectrum³, centered at characteristic wavelengths given by:

$$\lambda^m = (n_{co} - n_{cl}^m)\Lambda \quad (1)$$

In equation (1), λ^m is the m -th dip resonance wavelength, n_{co} and n_{cl}^m are, respectively, the effective refractive indexes of the core and of the m -th cladding mode and Λ is the grating period. Mechanical stress or temperature changes can modify both the grating period and the mode effective index. Moreover, external index changes can also lead to alteration in the effective index of the cladding modes. Such changes result in the wavelength shift of the attenuation dip (see equation 1). Some of the most interesting features of LPG for sensing applications are the possibility of real time response, quasi-distributed monitoring system with the use of several LPG in the same optical link, and information wavelength coded. This last feature results in a sensing system with no negative influence due to fluctuations in the source signal level.

In other hand, the environment preservation is one of the subjects that have received great attention from the society; the care with the correct use of water being one among the most emphasized ones. There are several ways to contaminate this natural resource, as, e.g., with industrial residues containing heavy metals. Among those metals Chromium can be a serious threat to human beings or cattle, depending upon its specification (in particular with regard to

the oxidation state), accumulated doses and on the concentration levels involved. In watercourses and reservoirs, the most common oxidation states of Chromium are Cr (III) or Cr (VI), which can enter the environment as a result of effluent discharge from industrial sources. Such sources can include, e.g., steel production, leather tanning, spray-painting operations and combustion sources. However, due to the high pollution level, residual wastewaters cannot be discharged directly into the sewers, and an on-line monitoring process becomes important for the environmental control. According to international standards, the maximum allowed contaminant level for total Chromium in drinking water is 0.05 mg/l.

Optical fiber sensors for the monitoring of Chromium in sewage water have been proposed by some authors^{4,5}. Their apparatus was based on the use of optical fiber absorption spectroscopy, and evanescent field absorption, respectively. The reported sensitivities are adequate for on-line monitoring, both for the total Chromium presence in the analyzed sample⁵ as for the detection of Cr (III) or Cr (VI) in concentration below the maximum allowed contaminant level for safe human use of water⁴.

This work shows the use of a long period grating as a sensing device to both detect the presence and distinguish between the Cr (III) and Cr (VI) oxidation states in water solutions.

2. EXPERIMENTAL SET-UP

The LPG is produced using a point-to-point writing method⁶, by applying an electrical arc discharge from a fusion splicer (Siemens, model S46999-M7A-71) on a standard telecommunication optical fiber⁷. The electrical arc parameters are 12 mA current and 0.5 s discharge time, producing a LPG with 65 interaction points, pitch of 595 μm and 38.7 mm long.

The characterization set-up is shown in figure 1. The optical fiber with the LPG is inserted through a glass recipient, where the liquid samples can be placed. In one of the sides, out of the recipient, the fiber is fastened onto a holder. After passing a pulley, the opposite fiber side is bound to a small box with a 20 g weight to keep the LPG under a constant longitudinal stress during the measurements. The optical source is a superluminescent LED with a 52 nm wavelength bandwidth centered at 1550 nm, and the reading system uses an optical spectrum analyzer (OSA) Anritsu model MS9710B with a 0.07 nm resolution and ± 5 pm of wavelength stability, plus a PC.

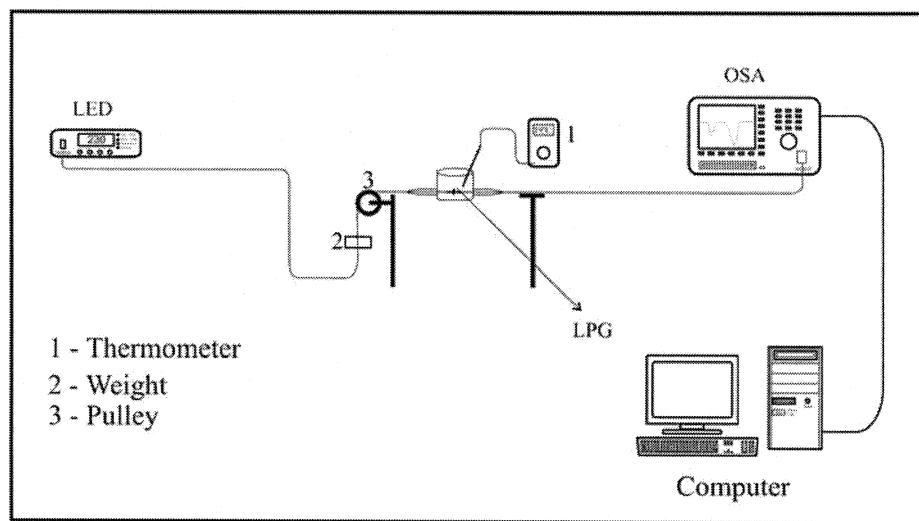


Figure 1: Experimental set-up employed to analyze the Chromium solutions.

To carry out the measurements, the samples of Cr (III) or Cr (VI) solutions are inserted into the recipient and the LPG transmission spectrum is measured. The central wavelength of the attenuation bands is obtained by adjusting a Gaussian line-shape to the experimental data. For both Chromium oxidation states, solutions with four different

concentrations are analyzed: 5.2, 2.6, 1.3 and 0.16 mg/l. A thermocouple is employed to monitor the temperature during the whole experiment, which is within 24.5 and 25.5 °C.

3. RESULTS AND DISCUSSION

Figure 2 shows the behavior for the main LPG attenuation dip in the presence of Chromium solutions with different concentrations. As can be seen from that figure, increasing in the concentrations of both Chromium oxidation states results the LPG attenuation peak shifts towards higher wavelengths. Samples with Chromium concentrations from 0.16 to 5.2 mg/l are analyzed, leading to maximum wavelength shifts (relative to the LPG in pure water) of 0.14 nm and 0.26 nm for Cr (III) and Cr (VI), respectively. Lines connecting the experimental points correspond to the best fit for the empirical equation $y = a - b.c^x$, where y is the LPG dip wavelength (nm), and x is Chromium concentration (mg/l). For the Cr (VI) adjust (solid line), $a = (1542.18 \pm 0.007)$ nm, $b = (0.2891 \pm 0.0136)$ nm, and $c = 0.5$. For the Cr (III) adjust (dashed line), $a = (1542.066 \pm 0.014)$ nm, $b = (0.15426 \pm 0.02856)$ nm, and $c = 0.5$. A comparison between the results obtained for both solutions shows that is possible to identify any of the Chromium oxidation states present in the sample until a lower limit concentration of 2.6 mg/l for the employed set-up. From that concentration and towards lower ones the errors of both measurements overlap, although it is possible to see that the wavelengths converge to the same value, 1541.92 nm. Table 1 summarizes the results obtained for the different concentrations of solutions.

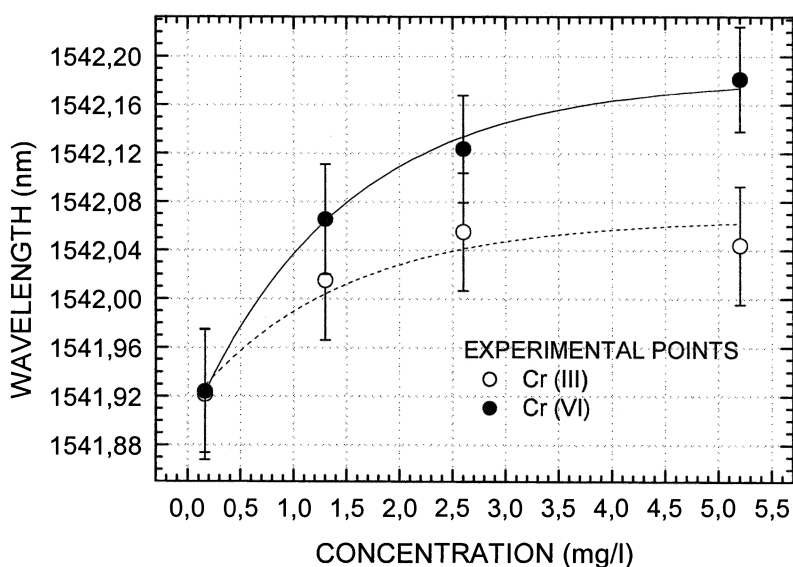


Figure 2: LPG attenuation dip behavior for solutions with different concentrations of the Cr (III) and Cr (VI). The lines connecting the points correspond to empirical curves.

Table 1: Measured LPG wavelength main dip for different Cr (III) and Cr (VI) concentrations in water.

Concentration (mg/l)	Wavelength (nm) Cr (III) solution	Wavelength (nm) Cr (VI) solution	Difference between the wavelengths (nm)
5.2	1542.05	1542.18	0.13
2.6	1542.04	1542.12	0.08
1.3	1542.01	1542.06	0.04
0.16	1541.92	1541.92	0.00

4. CONCLUSIONS

The results obtained in this work point to the prospect of using the LPG as a sensing device to detect the Chromium presence in water solutions, besides its concentration measurement. Furthermore, the sensor makes possible to distinguish between the oxidation states Cr (III) and Cr (VI) in such solutions, which is an important feature as Cr (VI) oxidation state is harmful to health and can lead to several diseases. In the environment preservation field, the optical device can be used to detect the Chromium presence in industrial residues, or to monitor the industrial conversion process of the harmful oxidation state Cr (VI) in Cr (III). An important feature of the proposed sensor to monitor industrial processes or for environment preservation is that the measurement process can be carried out on line, as the sensing response is very fast. The possibility of writing several sensors wavelength multiplexed in the same optical fiber allows establishing a sensing link covering a wide area, making possible a quasi-distributed monitoring process. In this work, the lower Chromium concentration limit to distinguish between the oxidation states is 2.6 mg/l. This limit can be shifted towards lower values by improving the LPG spectral sensitivity, which in turn can be achieved by writing gratings with lower bandwidths, or by using a cascade long-period structure. A further improvement in the sensor performance can be obtained by employing better measurement equipments (e.g. an optical spectrum analyzer with 1 pm resolution).

4. ACKNOWLEDGEMENTS

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