Cascade Long-Period Grating Structure for Cr (III) and Cr (VI) Detection in Water Environment

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***Abstract* — This works shows a fiber grating optical sensor that can be used to detect the presence of Cr (III) and Cr (VI) oxidation states in water solutions. The sensing device is a set of two in-series long period gratings produced in a standard telecommunication optical fiber by applying a suitable number of point-to-point electrical arc discharge 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 temperature, and the Chromium solution samples are added to it. In the range of concentrations analyzed (from 0.32 to 2.6 mg/l), the results show that is possible to distinguish between the two-oxidation states.**

***Index Terms* — Chromium, chemical industry, optical fiber devices.**

I. Introduction

Chromium in the nature is found in the oxidation states Cr (III) and Cr (VI). While the former is considered essential for the living organisms, the can be a serious threat for the health. According to international standards, the maximum of total Chromium in drinking water is 0.05 mg/l. The main source of environment contamination courses without an adequate treatment. These harmful factors accounts for the need for a rigorous control of such wastes, before it can be discharged in the environment. So, the information about the presence, amount and the oxidation states of the Chromium is very important for several industrial processes and water treatment. Most of the methods available to determine the presence of metals in water are quite complex to be used in routinely analyses, what makes the development of a simple way to measure both the amount and the oxidation state of the Chromium in water an important subject.

Optical fiber sensors for the monitoring of Chromium in sewage water have been proposed by some authors [1]-[2]. 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 total Chromium presence in the analyzed sample [2] as for the detection of Cr (III) or Cr (VI) in concentration below the maximum allowed contaminant level for safe human use of water [1]. This works shows the use of a sensing head with two in-series long period gratings as a sensing device to measure the concentration of Cr (III) or Cr (VI) oxidation states in water solutions.

II. Experimental Set-up

The two in-series LPG are produced using a point-by-point writing method [3], by applying an electrical arc discharge from a fusion splicer (Siemens, model S46999-M7A-71) on a standard telecommunication optical fiber [4]. The electrical arc parameters are 12 mA current and 0.5 seconds discharge time, producing gratings with 50 interaction points, pitch of 595 μm, 29.7 mm long and 3 dB of maximum attenuation. In the cascade structure, the two gratings are positioned 4 cm apart.

As a result of writing two in-series long period gratings apart a few centimeters in the same fiber, an interference fringe pattern is seen in the attenuation band [5]. Light coupled from the core to the cladding by the first LPG experiences a phase delay due to the different effective refractive index. Reaching the second LPG, the light is coupled back to the core, where it undergoes an interference with the remaining light from the first grating, resulting in the characteristic pattern. As the fringes present narrow bandwidths when compared with the bandwidths of the individual gratings, the wavelength of attenuation bands can be better identified, resulting in higher resolution measurement when compared with the conventional gratings. The resulting multiple attenuation-bands pattern is shown in the figure 1.

The characterization set-up is shown in the figure 2. The optical fiber with the LPG in-series 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 cantered 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.

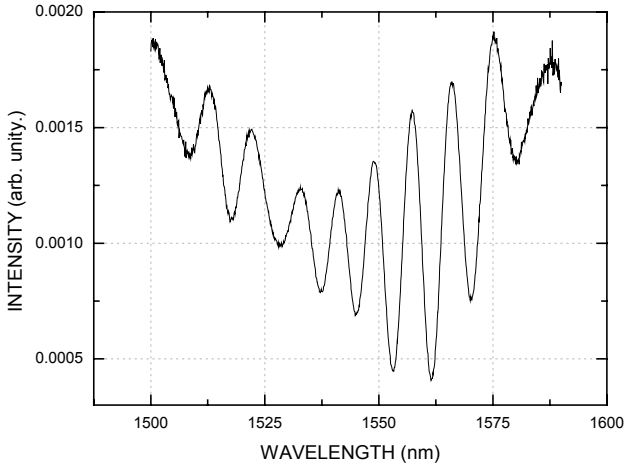

Fig. 1. Cascade LPG structure transmission spectrum

To minimize the influence of the temperature changes in the experiment, the thermal sensitivity of the seven dips in the transmission spectrum of the cascade LPG were measured, and the fifth dip (1543.6 nm), which presented the lowest temperature sensitivity (0.9 nm/ºC) was chosen to analyze the Chromium solutions. In these measurements, LPG transmission spectrum is measured in the presence of Cr (III) or Cr (VI) samples solutions with 50 ml of volume. For both Chromium oxidation states, solutions with four different concentrations are analyzed: 2.6, 1.3, 0.65 and 0.32 mg/l. A thermocouple is employed to monitor the temperature during the whole experiment, which is within 24.5 and 25.5ºC.

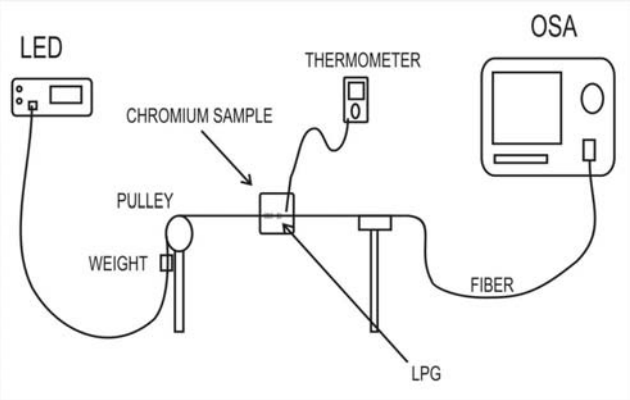

Fig. 2. Experimental set-up employed to analyzed the Chromium solutions

III. RESULTS AND DISCUSSION

Figure 3 shows the behavior for the 5th LPG attenuation dip in the presence of Chromium solutions. Cr (III) and Cr (VI) samples with concentrations from 0.32 to 2.6 mg/*l* were analyzed. Lines connecting the experimental points correspond to the best fit for the empirical equation $y = a + bx$, where y is the LPG dip wavelength (nm), and x is Chromium concentration (mg/*l*). For the Cr (VI) adjust (solid line), a = (1539.74 ± 0.01) nm and b = (0.02 ± 0.01) nm *l*/mg. For the Cr (III) adjust (doted line), a = (1539.64 ± 0.01) nm and b = (0.02 ± 0.01) nm *l*/mg. The obtained results show that is possible to distinguish between the two-oxidation states in the whole range of Chromium concentrations used in the experiment.

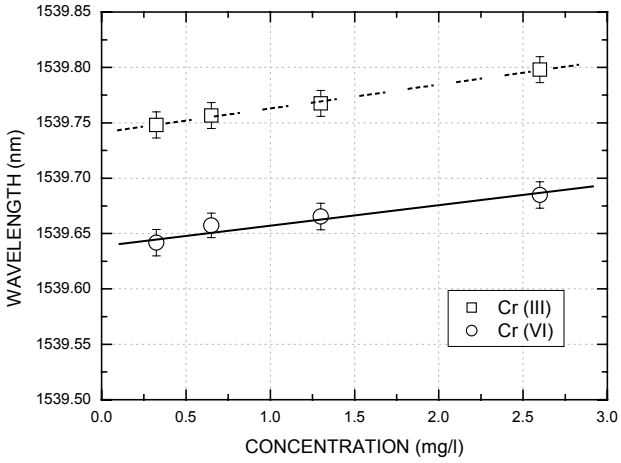

Fig. 3. LPG attenuation dip behavior for solutions of the Cr (III) and Cr (VI) with different concentrations

IV. CONCLUSIONS

The results presented in this works show that the use of cascade LPG leads to a better determination of central wavelength of dips in the grating transmission spectrum,, when compared with the results obtained for one LPG alone. This better resolution in turns allows making a more precise determination of the chromium concentration in the samples.

Furthermore, the sensor makes possible to distinguish 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 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. The device showed to be able to distinguish between the two-oxidation states in the whole range of Chromium concentration used in this work. The lower limit (0.32 mg/l) is eight times less than the lower limit that can be distinguish under the same experimental conditions but when only one LPG is used in the sensor [5]. For both Chromium oxidation states, the device sensitivity was (0.02 ± 0.01) nm *l*/mg.

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