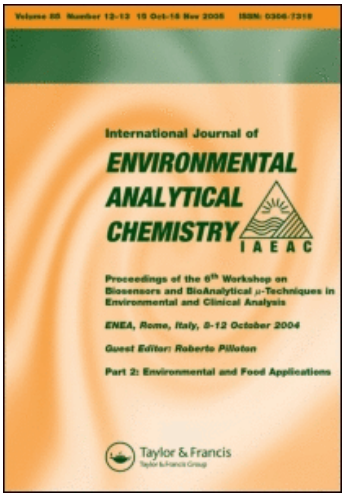

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On the Use of the Optothermal Window Technique for the Determination of Low Concentrations of Chromium (VI) and Phosphorus in Water

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ON THE USE OF THE OPTOTHERMAL WINDOW TECHNIQUE FOR THE DETERMINATION OF LOW CONCENTRATIONS OF CHROMIUM (VI) AND PHOSPHORUS IN WATER

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In this work we report about the use of the Optothermal Window (OW) technique, actually a variant of Photoacoustic Spectroscopy, combined with well-proven colorimetric methods to the determination of low concentrations of pollutants in water. As a first approach, chromium (VI) and phosphorus were determined in distilled water samples. The determination of Cr (VI) and P species in environmental and biological systems is currently of considerable interest due to the toxicity of their compounds to live organisms. Their maximum allowed values in drinking water were well discriminated in our experiments as well as the limits of optical spectrophotometric measurements. The detection limit in our measurements was 0.1 μmol/L P-PO_4^{3-} for phosphorus at 632.8 nm and 0.2 μmol/L for chromium (VI) at 514 nm.

Keywords: Optothermal window; water pollutants; chromium (VI) and phosphorus

INTRODUCTION

With the increasing human awareness in environmental problems, the detection of pollutant elements in water has become of increasing importance. In order to achieve higher sensitivity and selectivity than those of the traditional optical

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spectroscopic methods, the use of photothermal (PT) techniques is advantageous. These techniques enclose a group of high sensitivity methods[1]based on a photoinduced periodical change in the thermal state of a sample. Light energy absorbed and not lost by reemission leads to sample heating, which induces changes in temperature dependent sample parameters. The measurement of these changes is the basis of the PT methods. Among them, the Optothermal Window (OW) technique[2], actually a variant of conventional Photoacoustic Spectroscopy (PAS)[3], is especially suitable for spectroscopic studies of strongly absorbing liquids. In comparison to conventional PAS, the OW method offers some attractive features: First, the requirement for accommodating the sample in a sealed cell is no longer an impetus and the manipulation (loading and replacing) of the sample is simpler to perform. In addition, the OW signal remains unaffected by the thermal expansion of the sample. Finally, as long as it exceeds the sample thermal diffusion length (see later), the thickness of the sample is not relevant, making the technique more practical for quantitative analysis. On the other hand, in conventional Optical Spectrophotometry, the values of absorbance normally range between 0.01 and 2. Since the absorbance is proportional to the optical absorption coefficient, the range of detection of this parameter is limited. The OW overcomes this restriction due to the fact that the thermal diffusion length in the sample, which can be modified by choosing properly the light modulation frequency, determines the effective thickness being investigated. In this work we report the use of the OW technique combined with well-proven colorimetric methods to the determination of low concentrations of pollutants in water. As a first approach, the Optothermal Window Technique was used to measure the concentrations of chromium (VI) and Orthophosphates dissolved in distilled water. The determination of chromium species, especially Cr(VI) in environmental and biological systems is of considerable importance due to the essentiality or the toxicity of chromium compounds to live organisms. Cr(VI) is reported to be toxic due to its oxidizing capability and adverse impact on lung, liver and kidney. The United Nations Food and Agriculture Organization recommended maximum level of Cr(VI) for irrigation waters is 100 mg/L and the U.S. EPA primary drinking water standard MCL is 0.1 mg/L for total chromium[4]. The determination of phosphorus is as well of major concern due to the correlation with agricultural and industrial activities that may be responsible for an increase of phosphorus concentration in surface and ground waters, thus compromising the quality of the drinking water supply, principally due to the relation of phosphorus concentration with eutrophication processes. The phosphorus concentration range in waters is very large and detection of values ranging from 0.1 μmol/L $[PO_4^{3-}]$ (for sea water) to hundreds of μmol/L $[PO_4^{3-}]$ (for discharge streams) is necessary. For most applications, total phosphorus detection sensitivity better

than 10 mmol/L [PO_4^{3-}] is often required[5]. The above values for chromium and phosphorus are well resolved in our experiments as well as the detection limits of Optical Spectrophotometry.

EXPERIMENTAL

The experimental arrangement for OW measurements is ilustrated in Figure la. It includes a light source, whose radiation is modulated at the frequency f=1Hz by a mechanical chopper, constructed using a 120 steps motor and a digital circuit. Two diaphragms are used to reduce the diameter of the laser beam so that it enters (from below) and passes unobstructedly through the OW cell. This cell is well described by several authors[2,6–9] and it is shown schematically in part b of the Figure 1. It comprises an optically transparent sapphire disk (monocrystaline α-Al_2O_3) of thickness l_w=500 μm with an annular PZT piezoelectric transducer bonded to one of its faces. The other side carries the sample with the help of a silicon rubber O'Ring. Due to the absorption of radiation, the sample temperature rises and the generated heat diffuses into the disc that expands. The induced stress is transmitted to the PZT, inducing an electrical signal. This signal is amplified by a home made low noise preamplifier (gain 100) and measured by an EG&G Lock-In amplifier interfaced by a personal computer. The whole measuring system is mounted on an antivibrational table and care was taken to avoid temperature changes during each measurement. The cell is easy to clean and to align. Both, the alignment and the unavoidable background signal level were regularly checked between successive measurements and following each clean up of the cell.

THEORETICAL ASPECTS

The optothermal signal is obtained from the solution of the heat conduction equation in the sample and detector. Assuming that the liquid is thermally thick and the window is thermally thin for the used modulation frequency, the signal normalized value is given by[8,9]

$$S = \frac{\beta\mu_s}{\beta\mu_s + 1 + j}, \tag{1}$$

where β is the optical absorption coefficient, $j=(-1)^{1/2}$and $\mu=(\alpha/\pi\otimes)^{1/2}$ is the thermal diffusion length. Here α is the thermal diffusivity and f is the modulation frequency. The normalisation is made relative to a measurement on a

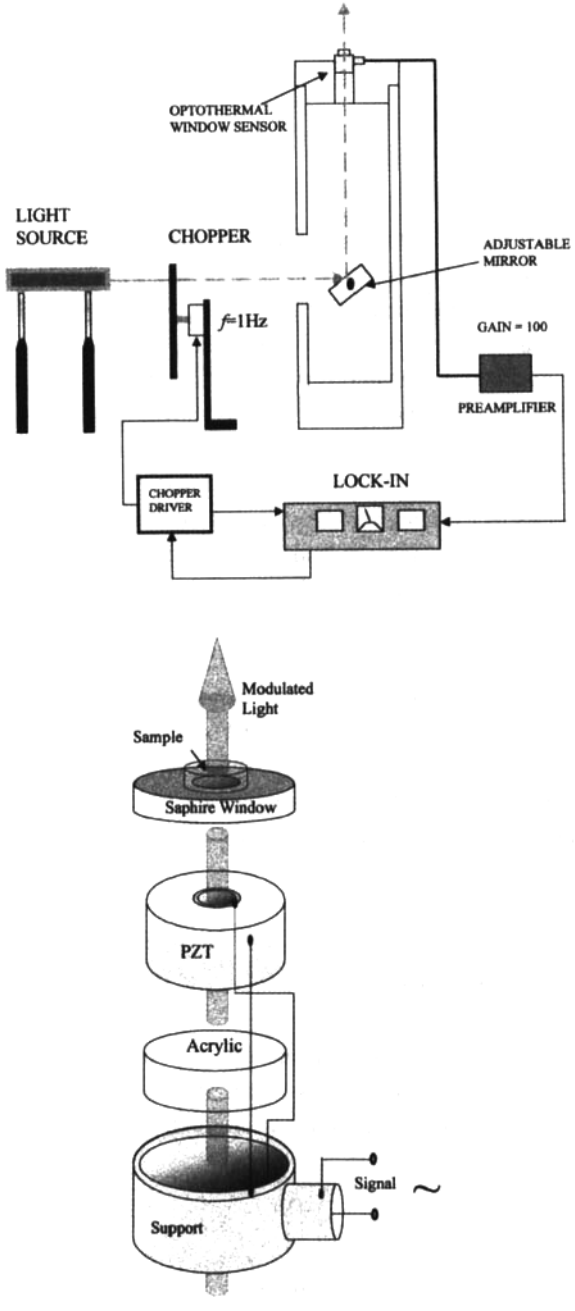

FIGURE 1 (a) Experimental arrangement for OW measurements. (b) Schematic view of the OW sensor

strongly absorbing sample such as black drawing ink. The amplitude of Eq. (1) is given by

$$A = \frac{\beta\mu_s}{\sqrt{(\beta\mu_s + 1)^2 + 1}} \tag{2}$$

and its phase by

$$\varphi = \tan^{-1}\left(\frac{1}{\beta\mu_s + 1}\right). \tag{3}$$

As we can see, the signal depends on the temperature fluctuation taking place in the sample within a depth μ_s of one thermal diffusion length from the sample-window interface. This layer of thickness μ_s defines the effective length of the experiment. As one can see, for water (α_s=0.00145 cm^2/s) at a frequency f=1Hz, the thermal diffusion length becomes μ_s=215 μm. Taking into account that low concentrations of P and Cr (within the ppm-ppb level) do not change drastically the value of the thermal properties of water, only a small amount (a drop) of liquid sample is necessary to achieve the condition $\mu_s < l_s$, where l_s is the sample thickness. Note that the OW signal is independent of the values of l_s, as shown by equations (1) to (3), in evident contrast with optical spectrophotometry, for example, in which the sample thickness, generally of the order of 1 cm or more, is necessary to calculate the sample optical absorption coefficient.

The normalization condition for the measured signal is the optical saturation, i.e., when $\beta\mu_s$ is large, leading to A=1 and φ=0 deg. For small $\beta\mu_s$ values the amplitude becomes

$$A = \frac{\beta\mu_s}{\sqrt{2}}, \tag{4}$$

i.e., a linear operating regime and the phase shows a saturation (φ=-45 deg). In this regime one can relate the OW signal to the molar sample concentration C through the sample molar extinction coefficient χ. Taking into account that the sample absorbance a is defined as

$$a = (\beta l) log_{10} e = \chi C l, \tag{5}$$

where l is the optical path, then, from Eq. (4) we have

$$A = \frac{C\chi}{0,434}\sqrt{\frac{\alpha_s}{2\pi f}}. \tag{6}$$

SAMPLE PREPARATION AND METHODOLOGY

A series of calibration samples was prepared using a suitable and well proven colorimetric procedure and standard samples, obtaining a broad absorption band

centred near the light wavelength available for our experiments. Distilled water was used as solvent and distilled water with reagents served as reference blank samples. For chromium (VI) determinations, the 1,5 diphenylcarbazide method[4] was chosen and for phosphorus, the ammonium molybdate/potassium antimonyl tartrate with ascorbic acid as the reductor agent method[10] was applied. All solutions were prepared using analytical-reagent grade chemicals and deionised water. Optical Spectrophotometric measurements show an absorption band centred at 885 nm followed by a lower intensity peak at 611 nm for phosphorus solutions and a band at 540 nm for Cr (VI) solutions. We have used therefore as excitation wavelengths the 632.8 nm line of a 20 mW Meredith Instruments He-Ne laser, and the 514 nm line of 100 mW tunable Ar ion laser (Omnichrome 543-MAP), for measurements of P and Cr in water respectively.

The value of β can be determined by several means as described by Helander[8]. We have resorted to use the amplitude of the signal (Eq. (2)) since no adjustment of the phase angle is required. For each sample this magnitude was measured and the values corresponding to a blank solution were subtracted. The results were then normalized to data obtained from black drawing ink. For comparison purposes and to show the advantages of the OW method with respect to the spectrophotometric ones, we have made optical absorbance measurements for each sample at the excitation light wavelength. The results of our measurements will be discussed below.

RESULTS

Phosphorus

The sensitivity and linearity of the OW detected phosphate molybdenum blue colorimetry method was tested using a dilution series of freshly-made phosphate standard solutions. The normalized amplitude of the OW signal from samples whose concentration varies between 0.1 and 200 μmol/*L* P-PO_4^{3-} is shown in Figure 2. As one can see in the logarithmic representation for P measurements, at low concentrations the signal shows saturation. It is limited by the residual absorption of the blank solution and not by the OW method sensitivity.

The solid line in Fig. 3 represents the theoretical calibration curve $A(\beta)$ calculated by means of Eq. (2), with the parameter μ_s =215 μm as discussed above. The values ε_w=9900$Ws^{1/2}m^{-2}K^{-1}$ and α_w=1.09×$10^{-5}m^2/s$ were used for calculations[9]. The position of the experimental points on this curve are determined

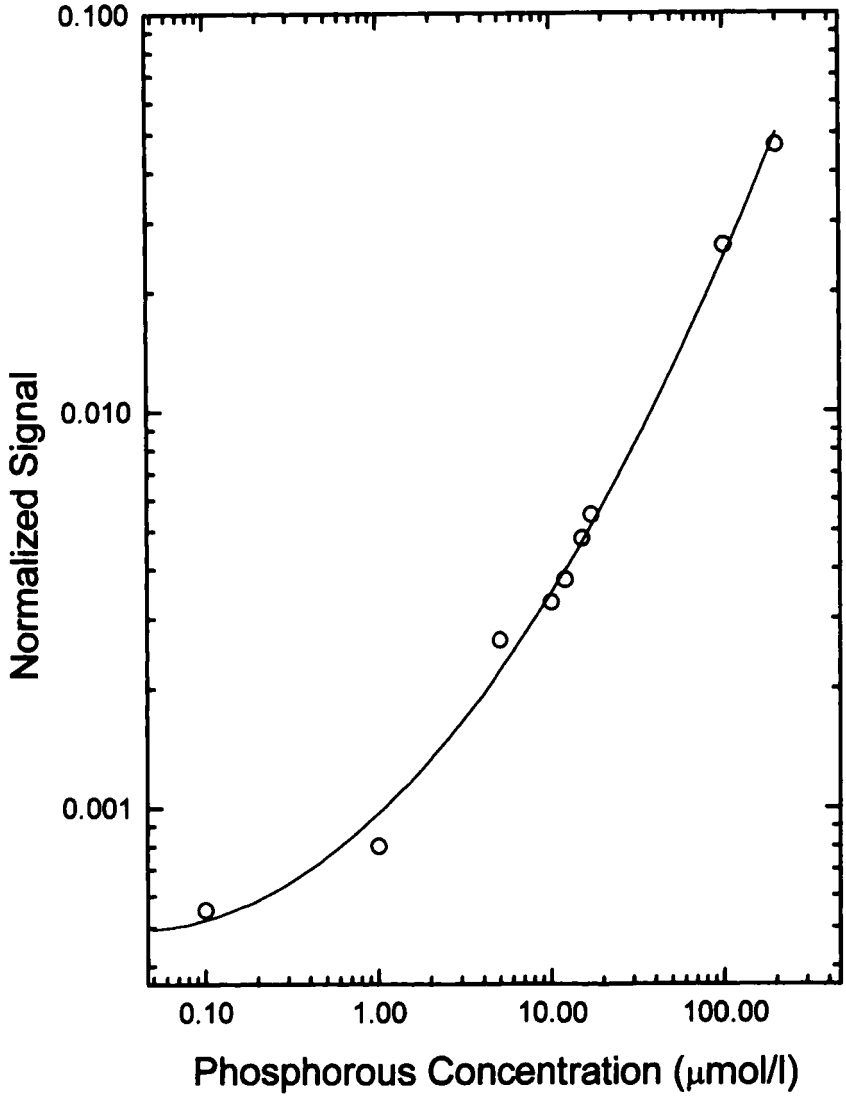

FIGURE 2 Normalized amplitude of the OW signal as a function of the phosphorus concentration in water

by the A co-ordinate and the corresponding β values can be read directly on the graph or can be computed by inversion of Eq. (2).

In Figure 4a we show the measured absorbance values at 632.8 nm (with an UV-160A Shimadzu Ultraviolet-Visible Spectrophotometer) as a function of the

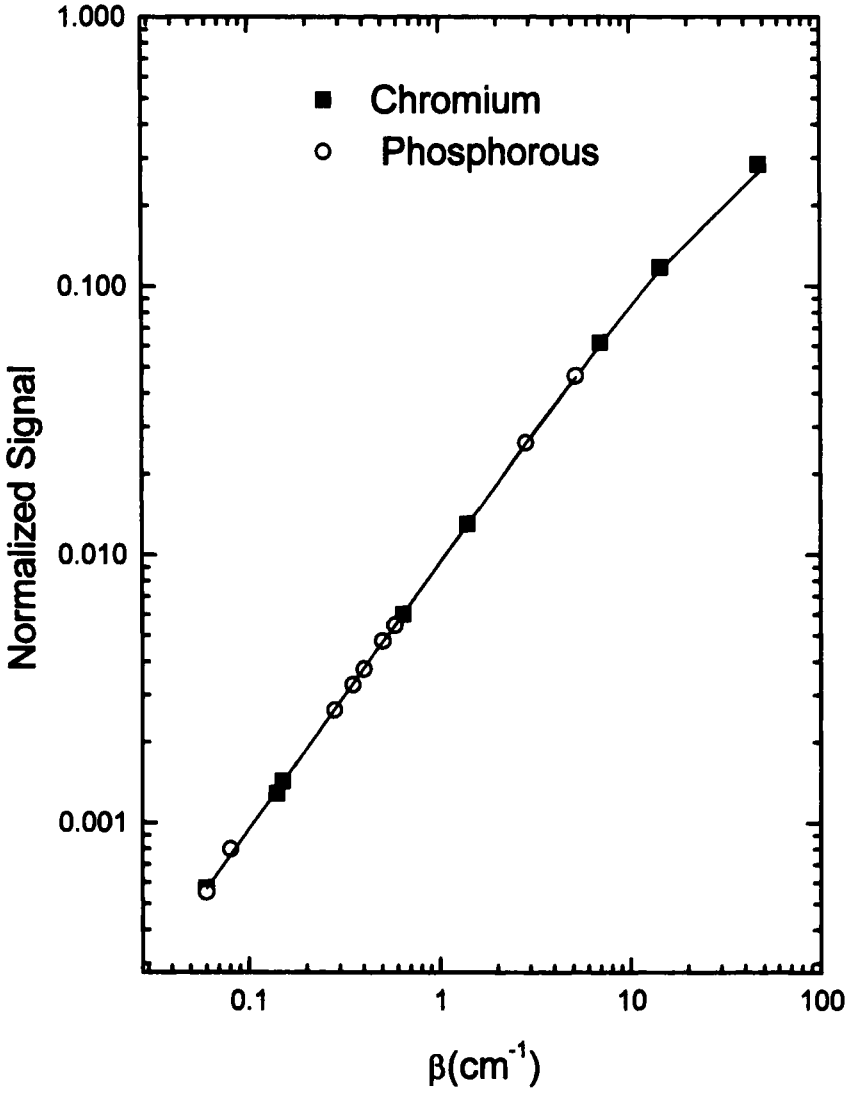

FIGURE 3 Normalized amplitude of the OW signal as a function of the optical absorption coefficient. The solid line represents the theoretical dependence calculated after Eq. (2). The circles and the squares are the measured amplitude values for P and Cr(VI), respectively

phosphorus sample concentration in the range from 10 to 18 μmol/*L*. Lower concentrations were not possible to be measured by this conventional technique. The solid line in the figure is the best fit result of the data to Eq. (5), taking the molar extinction coefficient χ as adjustable parameter (note that we have used a cuvete

of thickness l=1 cm for optical spectrophotometric measurements). We have obtained the value $\chi=(0.0077\pm0.0008)\times10^6$ $L\text{mol}^{-1}\text{cm}^{-1}$. A similar analysis was made using the OW results. The solid line of Fig. 4b shows the best fit of the experimental data to Eq. (6), taking also χ as adjustable parameter. The result $\chi=(0.0066\pm0.0002)\times10^6$ $L\text{mol}^{-1}\text{cm}^{-1}$ was thus obtained. A good agreement was obtained between the results given by the two methods. As we can see, in the case of the OW technique the determination of the molar extinction coefficient is made with more experimental points and in a greater concentration range (0.1 to 200 μmol/L). No reported value for this magnitude at 632.8 nm was found in the literature.

Chromium (VI)

The sensitivity and linearity of the OW detected chromium(VI)-1,5 diphenylcarbazide colorimetry method was tested using dilution series of freshly-made chromium (VI) standard solutions. The normalized amplitude of the OW signal from chromium (VI) samples with concentrations between 0.02 and 1000 μmol/L is shown in Figure 5, showing the saturation at low concentrations.

In Figure 3 the position of the experimental points on the theoretical curve A vs β are also represented. As in the case of phosphorus the corresponding β values can be read directly on the graph.

In Figure 6a we show the measured absorbance values as a function of sample concentration in the range where Optical Spectrophotometry leads to a non-saturated signal at 514 nm. The solid line in the figure is the best fit result of the data to Eq. (5), giving the value $\chi=(0.0227\pm0.0006)\times10^6$ $L\text{mol}^{-1}\text{cm}^{-1}$. The solid line in Fig. 6b shows the best fit of the experimental data to Eq. (6), taking also χ as adjustable parameter. The result $\chi=(0.0168\pm0.0003)\times10^6$ $L\text{mol}^{-1}\text{cm}^{-1}$ was thus obtained. The results obtained by both methods, the OW and the optical spectrophotometry, are of the same order of magnitude, showing the potential of the former to perform spectroscopic measurements in liquids. For comparison, the literature reported value is $\chi=0.0400\times10^6$ $L\text{mol}^{-1}\text{cm}^{-1}$ at 540 nm[4], where the light absorption is approximately twice the value at 514 nm.

DISCUSSION

As discussed by Bicanic et al[5], the widely used molybdenium blue colorimetry technique combined with a standard optical spectrophotometry is restricted to concentrations higher than 10 mmol/l. On the other hand, the detection limits of

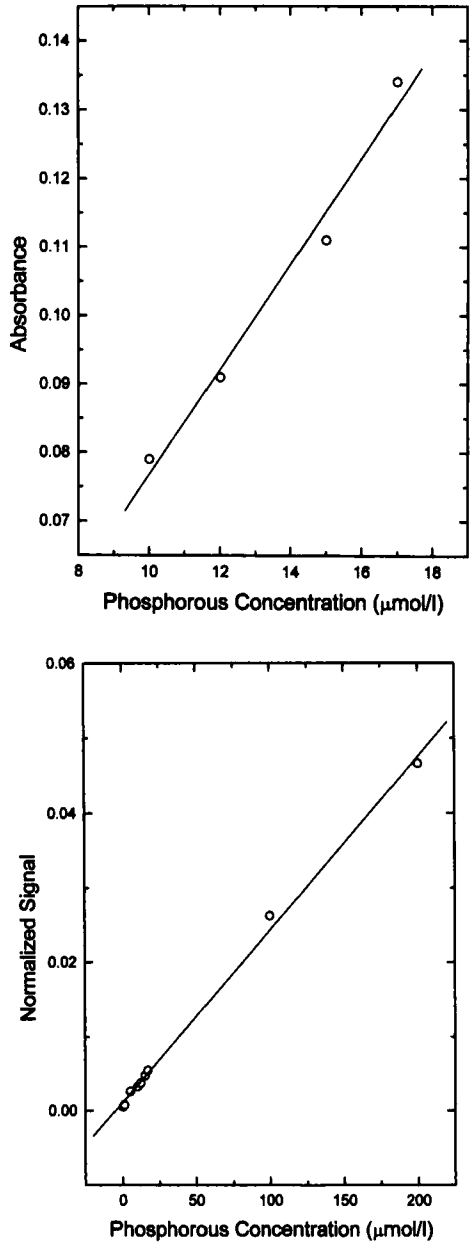

FIGURE 4 a) Optical Absorbance as a function of phosphorus concentration. The solid curve is the best fit of the data by means of Eq. (5). b) Normalized amplitude of the OW signal as a function of the P-Concentration in water. The solid line in part (b) represents the best fit of the experimental data to Eq. (6)

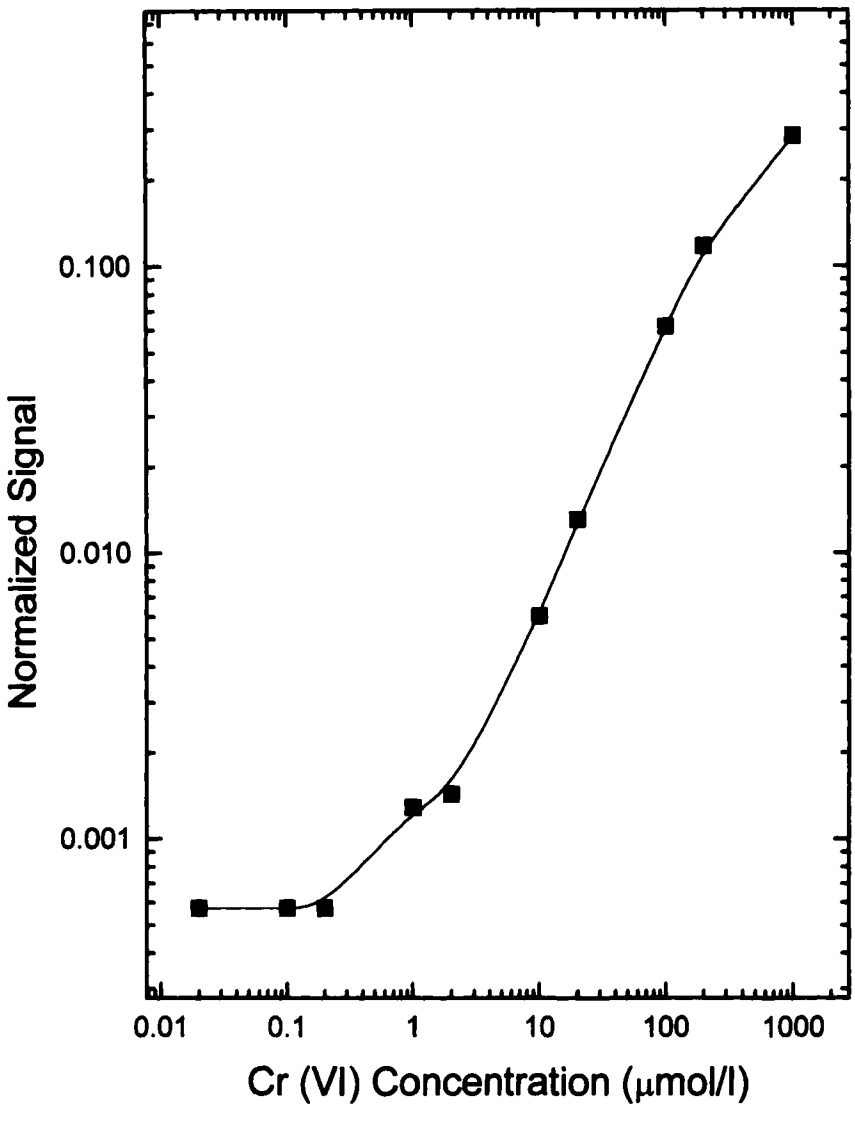

FIGURE 5 Normalized amplitude of the OW signal as a function of the Cr (VI)-concentration in water

phosphate in water using ion-selective eletrodes and other sensors are much above 10 mmol/l. Infrared absorption spectroscopy cannot be used for low level detection of phosphates due to overlapping of their absorption bands with those of water, In the last years some attempts were made to apply PT techniques to

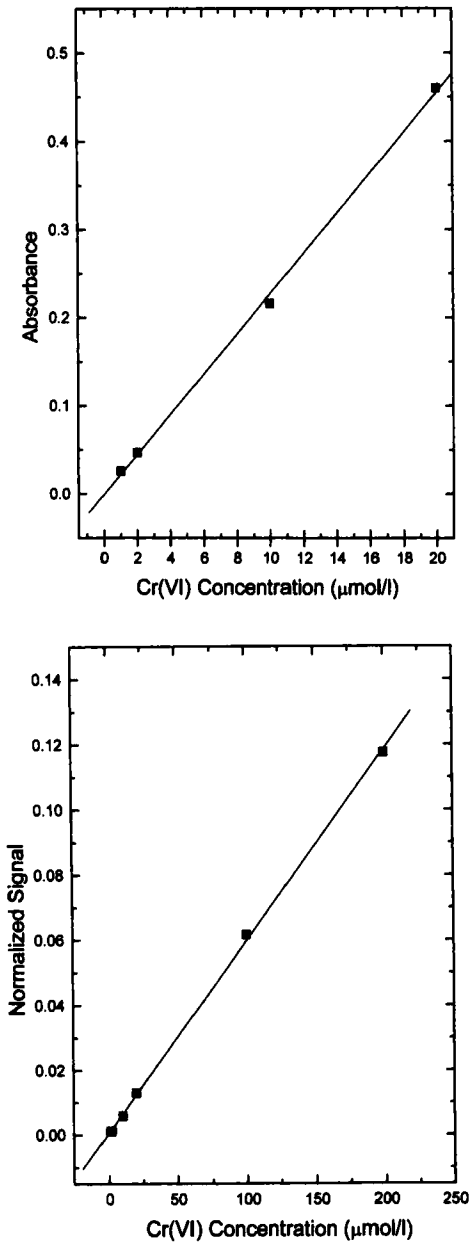

FIGURE 6 a) Optical Absorbance as a function of Cr (VI)-concentration. The solid curve is the best fit of the data by means of Eq. (5). b) Normalized amplitude of the OW signal as a function of the Cr (VI)-concentration in water. The solid line in part (b) represents the best fit of the experimental data to Eq. (6)

detect low levels of P in water. Using a piezophotoacoustic detector scheme Bicanic et al[11] were able to improve the sensitivity to 1 mmol/L. A detection sensitivity of 0.1 mmol/L of PO_4^{3-} has been achieved by Bicanic et al[5] using a collinear photothermal beam deflection technique. The detection limit in our measurements was 0.1 μmol/L P-PO_4^{3-} and the normalized OW signal showed to be linear up to 200 μmol/L P-PO_4^{3-}, showing that reliable colorimetric determination of phosphate by means of the Optothermal Window Technique is possible for a large range of phosphorous concentration in water.

Chromium (VI) determinations in water have been performed by several techniques. The most reliable technique for chromium determination in water is actually the ICP-AES. By using this technique, McLeod et al[12] were able to determine up to 0.20 μgl/L of Cr (VI) in a flow injection system. Subramanian[13] using Furnace Atomic Absorption Spectroscopy achieved a detection limit of 0.3 μg/L of Cr (VI) in a steady state system. Welz et al[14] using Flame Atomic Absorption Spectrometric Detection with a flow injection system found the detection limit for Cr(VI) to be 0.8 μg/L. All the above techniques are well established and normally are applied for total chromium determinations. However, these techniques require some means of separation prior to the measurement in order to distinguish different species of the same elements in case of Cr(VI) and Cr(III). Our results showed a detection limit of 0.2 μmol/L (10 μg/L) for Cr(VI), being this value lower than the maximum allowed value of Cr(VI) in drinking water.

The well-proven colorimetric methods used for phosphorus and chromium (VI) are highly selective. The presence of some other ions might interfere, however, if present in high concentrations[4,10].

CONCLUSIONS

Low concentrations of chromium (VI) and phosphorus using standard solutions were determined using well established colorimetric methods and a variant of Photoacoustic Spectroscopy, namely the Optothermal Window technique. The detection limits of Optical Spectrophotometry are well resolved in our experiments. In the case of phosphorus it is worth to notice that our measurements were made using an excitation wavelength somewhat different than those corresponding to the maximal absorption of the studied solutions. The use of an excitation wavelength nearer to 885 nm, using for example a semiconductor laser available on the market at low cost, is expected to be appropriate for enhancing the sensitivity of the OW method for the determination of phosphorus in water. For both,

Cr (VI) and P, the use of diode laser sources also leads to the possibility of constructing a compact OW device, suitable to perform in-field measurements. This work is a new step in demonstrating the possibilities of the OW technique to perform spectroscopic studies in environmental samples. This technique appears as a promising tool for such studies whenever excitation of the analyte can be achieved and the window transparency will be provided. This work also complement existing ones about the application of a combination of colorimetric and photothermal method to trace determinations in liquid samples.

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