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Spectrophotometric sensor system based on a liquid waveguide capillary cell for the determination of titanium: Application to natural waters, sunscreens and a lake sediment

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ABSTRACT

An analytical procedure for the spectrophotometric determination of titanium at trace levels was developed. The procedure involves the use of a multi-pumping flow system (MPFS) coupled with a liquid waveguide capillary cell (LWCC) with 1.0 m path length, 550 μm i.d. and 250 μL internal volume, which enabled to enhance the sensitivity of the determination and thus avoid complex and time-consuming pre-concentration steps. The determination is based on the colorimetric reaction of titanium with chromotropic acid. The limit of detection (3σ) was 0.4 μg/L and a linear response up to 100 μg/L with a sample throughput of 46 h^{-1}, and a low reagent consumption/effluent production was achieved. The developed procedure was applied to natural waters, sunscreen formulations and one certified lake sediment sample.

1. Introduction

Titanium is the ninth most abundant element in earth's crust, a natural constituent of rocks, soils and sediments [1]. The levels of Ti in rocks are lower than 2% (w/w) [2]. The Ti concentrations found in riverine, estuarine and coastal waters range from 0.005 to more than 4.8 μg/L [3] and from 0.2 to 17 ng/L in ocean waters [1]. The Ti minerals are very resistant to chemical weathering in soil and sedimentary environments, allowing the common use of Ti as a guide element to compare the mobility of the different elements [1].

In recent years, Ti has acquired growing importance in several industrial fields because of its particular physical and chemical characteristics. The main commercially available compound, titanium dioxide, is used in solar energy cells [4], as a photocatalyst in sterilization, air cleaning and water purification processes [5,6], as an ingredient of sunscreens, cosmetics, toothpastes, paints and plastics, and in the manufacture of building materials, aircrafts and missiles [7,8]. It also shows great promise in the development of antitumor agents [9], and for drug delivery, environmental cleanup and computer manufacture [10]. Titanium dioxide nanoparticles also shows durable photocatalytic activity, induced by UV-light, causing photochemical degradation of organic compounds [6,11], suggesting a potential use in wastewater treatment plants [8].

TiO_2 in the form of nanoparticles is not considered as new materials, as bulk TiO_2 has been incorporated into various products as a white pigment for decades; it is therefore categorized as a new form of an existing substance. Nanoparticles are ultrafine particles with length in two or three dimensions greater than 1 nm and smaller than 100 nm [10,12]. Despite the large scale and increasing production of these materials, few studies have addressed the possible environmental threat posed by nanoparticles.

The nanoparticles toxicity differs with particle type, size, surface area and functional groups attached [6,12]. Oberdörster et al. revealed that the smaller the size of the nanoparticles, stronger the exerted toxicity is [13], although the relation between the physicochemical properties of nanoparticles and their toxicity appears to be more complex [14].

In a recent study [15], based on the already existing quantitative toxicity data (ex. LC_{50} or EC_{50}) for the evaluation of the potential hazardous effects of nanoparticles [16], TiO_2 was classified as "harmful". This classification is based on studies that involved different groups of organisms (crustaceans, bacteria, algae, fish, nematodes and yeasts) and concluded that algae are the most sensitive ones. In the case of bulk TiO_2 the toxicity falls into the same classification, showing a lowest LC_{50} value for algae, similar to the value found for the nanoparticles formulation.

The aquifers may be the principal receiver of nanotechnology industry discharges. Therefore, ecotoxicology studies on water col-

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umn organisms and across several taxonomic groups are of great interest for the comprehensive effect assessment of the nanoparticles in the aquatic environment [5,7,14,17,18].

The development of analytical methods focused on understanding the fate of nanoparticles in the aquatic environment is important, as the lack of detection/quantification tools hampers the advancements on other areas related to its toxicity.

In general, flow systems are very suitable for water analysis because of increased accuracy, good repeatability, low equipment cost, high sample throughput, simplified sample handling, reduced contamination risks, high degree of automation and reduction in sample/reagents consumption and effluent production [19,20].

Regarding flow methodologies for the determination of Ti, the majority are based on molecular absorption spectrophotometry [2,8,21,22], although there are some works exploiting other detection techniques such as chemiluminescence [23], ICP-AES [24] and ICP-MS [25].

The spectrophotometric procedures are simple, fast and robust and there are some colorimetric reagents used for titanium determination as chromotropic acid, tiron, sulfosalicylic acid [2] and 4,4′-diantipyrylmethane [21]. However, to reach the determination of titanium at trace levels with spectrophtotometric procedures, a preconcentration step is necessary [26], significantly increasing the complexity of the flow systems manifold and decreasing the determination rate.

To overcome these difficulties, in this work we propose the use of a liquid waveguide capillary cell (LWCC), a sample cell where the optical path length is increased without light attenuation [27], which enables to significantly increase sensitivity, in order to attain the direct determination (i.e., without a pre-concentration step) of trace levels of titanium in samples of different types (as natural waters, sunscreens and lake sediments). This approach was already successfully used in the determination of iron at low concentration levels [28]. The characteristics of this device permit total internal reflection of the light on the walls as the light conducting path is transparent to the wavelength of interest and has a refractive index higher than the walls material. Thus, light is kept in the optically denser core.

To carry out the in-line sample reaction needed for the spectrophotometric determination of Ti, an option was made for the utilization of a manifold based on the recently proposed multi-pumping flow technique. This is characterized by a pulsed flow capable of producing an improved sample/reagent mixing and reaction zone homogenization [29]. Multi-pumping flow systems (MPFS) use multiple low-cost solenoid micro-pumps strategically positioned in the manifold, which, when controlled by computer software, provide easy and versatile automated fluid handling operations. The solenoid micro-pumps require low-power supply voltage to work and have a small size when compared to peristaltic pumps, making it an advantageous alternative for portable equipment/in situ analysis.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with analytical reagent-grade chemicals and deionized water. Titanium (IV) stock standard solution (100 mg/L) was prepared by diluting the respective 1000 mg/L atomic absorption standard (Fluka, 04689) with 0.01 mol/L HCl solution. Calibrating solutions in the range of 10–100 μg/L were daily prepared by rigorous dilution of the Ti stock solution with 0.01 mol/L HCl.

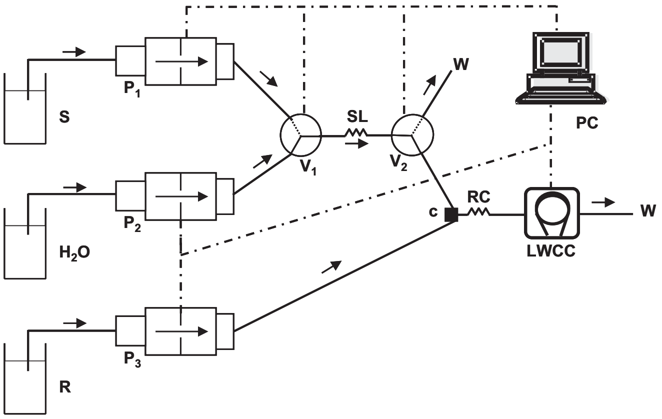

Fig. 1. Multi-pumping flow system for the determination of titanium. Pi, pumps; Vi, solenoid valves; SL, sample loop (200 μL); RC, reaction coil (50 cm); c, confluence; LWCC, detector (100 cm optical path, 425 nm); PC, computer; W, waste; S, sample or standard; and R, colour reagent (chromotropic acid) and buffer solution (acetate buffer with ascorbic acid).

A certified reference material (CRM), a lake sediment sample ref.ª IAEA-SL-1, was analysed in order to evaluate the accuracy of the developed analytical procedure.

Five sunscreen samples were also analysed by the developed method and the results obtained were compared with the alternative ICP MS procedure.

The TiO_2 nanoparticles (<100 nm) used in the recovery tests performed with the CRM sample were from Sigma–Aldrich (Ref. 634662).

The solutions used in interference studies were prepared by diluting commercial atomic absorption standard solutions (Spectrosol, BDH) of Fe, Al, Cu or Pb by dissolving the respective salts NH_4VO_3, $K_2Cr_2O_7$ and NaF (Merck), in the case of V, Cr and F.

Chromotropic acid colour reagent was daily prepared by dissolving 0.025 g of $C_{10}H_6Na_2O_8S_2{\cdot}2H_2O$ (Sigma–Aldrich) and 1.0 g of ascorbic acid (VWR International) in 100 mL of a 0.2 mol/L acetic acid–sodium acetate solution, resulting in a solution with 1.25 mmol/L and 0.113 mol/L of chromotropic acid and ascorbic acid, respectively.

2.2. Apparatus

The manifold used for the determination of Ti is shown in Fig. 1 and comprised three micro-pumps (Bio-Chem Valve Inc., Boonton, NJ, USA, Ref. 120SP1220 and 120SP1230), with nominal dispensing volumes of 20 and 30 μL per stroke, and two commutation valves (NResearch, Caldwell, NJ, USA, Ref 161T031) with an internal volume of 27 μL. To control both micro-pumps and commutation valves, an I/O digital card with eight optocoupled digital input channels and eight digital relay output channels was used. This card was connected to a personal computer through an RS485/RS232 interface and can independently control the operation of up to eight micro-pumps and/or commutation valves. These devices are set on a motherboard connected to a protection interface, which is connected to the relay outputs and an additional power source of 12 V is required to activate the solenoid devices. In order to minimize the heat generation and extend the lifetime of the valves, a solenoid protection system (Sciware, Mallorca, Spain) was used. The power source, the RS serial interface and the I/O cards were integrated into a unique module (Ref. Module1 Sciware). The volumes dispensed by the micro-pumps in each stroke were verified and are shown in Table 1.

For the solenoid valves, the exchange options were classified in on/off lines. The "on" line was assigned to the flow manifold and