



Titanium determination by multisyringe flow injection analysis system and a liquid waveguide capillary cell in solid and liquid environmental samples



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ABSTRACT

A multisyringe flow injection analysis system using a liquid waveguide capillary cell (MSFIA-LWCC) has been used for the spectrophotometric determination of titanium (Ti) in marine environmental samples. Samples were previously digested using potassium peroxodisulfate ($K_2S_2O_8$). The method showed to be linear over a range up to 1 μ M with a detection limit of 9.2 nM. The analysis consumes little reagent (250 μ L) and sample (600 μ L). It had an adequate accuracy with high repeatability (RSD of 1.8%) for all marine samples. The proposed method was used to evaluate the concentration of Ti in natural samples collected in the coastal area of the Majorca Island (Western Mediterranean Sea). We report average concentrations of Ti in coastal surface microlayer of 510.7 ± 267.2 nM, in surface sediments of 2.72 ± 1.84 μ mol/g, and in rhizomes and leaves of *Posidonia oceanica* of 310 ± 295 nmol/g and 157 ± 132 nmol/g, respectively.

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1. Introduction

Titanium is the fourth most abundant metal and the ninth most abundant element in the earth's crust (Carp et al., 2004). Dissolved Ti is present as a trace element in seawater at extremely low concentrations varying from few pM in open ocean to nM levels in coastal areas (Dammshäuser and Croot, 2012; Dammshäuser et al., 2011; Orians and Boyle, 1993; Orians et al., 1990; Skrabal et al., 1992; Yang et al., 1981; Yokoi and van den Berg, 1991). Main inputs of this element to coastal waters come from weathering, dust deposition, industrial and domestic wastewater discharges. Titanium dioxide (TiO_2) is used in a wide range of cosmetics and personal care products including sunscreen, makeup, bath soaps, etc. that are introduced in the coastal waters via direct release from the skin during swimming and bathing or by indirect way via wastewater treatment plants (Giokas et al., 2007). The input of TiO_2 in the coastal marine systems could be of potential of concern, because under natural UV radiation, TiO_2 nanoparticles can function as catalyst, which makes them an apparent strong oxidizing agent (production of reactive oxygen species: ROS) (Chen et al., 2012) and causing environmental toxicity. For example, Miller et al. (2012) indicated that TiO_2 , under low UV radiation can induce toxicity to marine phytoplankton. Because of its insolubility in

water, in nature, TiO_2 nanoparticles tend to accumulate in soils and particles (Botta et al., 2011).

Determination of TiO_2 in environmental samples requires strong acidic optionally microwave-assisted digestion prior to analysis or other digestion methods that use ammonium persulfate or potassium bisulfate to produce sulfate radicals being able to generate soluble Ti^{4+} salts because of its chemical weathering (Khosravi et al., 2012; Páscoa et al., 2011). A variety of analytical methods for the determination of dissolved Ti in environmental samples have been reported. Usually, Ti in seawater is analyzed by ion-exchange spectrophotometry (Capitán-Vallvey et al., 1989), catalytic cathodic stripping voltammetry (Croot, 2011; Yokoi and van den Berg, 1991) or inductively coupled plasma mass spectrometry (ICP-MS) with previous preconcentration on a chelating resin (Orians and Boyle, 1993).

A recently described method based on spectrophotometric detection using a liquid waveguide capillary cell (LWCC) automated in a multipumping flow system (MPFS) has demonstrated to be sufficiently sensitive for the analysis of Ti^{4+} in natural waters, sediments and sunscreens (Páscoa et al., 2011). The main advantages over the former technique is the low reagent consumption and waste production, the rapidness of analysis, automatic operation, robustness and the portability of the reported analysis system (Páscoa et al., 2012).

For seawater analysis, the highly saline matrix has further to be taken into consideration, inhibiting the use of mass spectrometric methods without prior matrix removal. In combination with the

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prior required digestion, sample preparation becomes very laborious. Therefore, there is an actual demand for economic, simpler, and especially more robust instrumentation, which can be applied directly to digested samples.

In this work, we developed a similar system based on the flow technique multisyringe flow injection analysis (MSFIA) and we demonstrate its efficiency for the analysis of Ti in liquid and solid samples from marine environment. The analytical method uses potassium peroxodisulfate ($K_2S_2O_8$) as disaggregation agent of TiO_2 to yield soluble Ti^{4+} . The method has been demonstrated to be effective for the analysis of Ti in three of the main compartment of the marine coastal system: coastal SML, marine sediments, and the marine macrophytes.

2. Materials and methods

2.1. Reagents

All solutions were prepared from analytical reagent-grade chemicals and ultrapure water. The chromogenic reagent was prepared as reported in a previously described method (Páscoa et al., 2011). It was prepared daily by dissolving 0.0187 g of chromotropic acid disodium salt dihydrate ($(OH)_2C_{10}H_4(SO_3Na)_2 \cdot 2H_2O$; Sigma–Aldrich) and 0.375 g of L(+) ascorbic acid (Scharlau) into 50 mL of 1.5 M sodium acetate buffer adjusted to pH = 4.6.

Titanium stock solution was prepared by diluting 1000 mg L^{-1} Ti ICP standard solution (Merck) with 0.1 M HNO_3 suprapure (Merck). Calibration standard solutions in the range of 10 nM to 1.0 μ M were prepared by appropriate dilution of the Ti stock solution in 0.1 M HNO_3 suprapure quality.

Extra-pure potassium peroxodisulfate ($K_2S_2O_8$) was purchased from Scharlau Chemie and used for the sample digestion to yield reactive Ti^{4+} as described in Section 2.3.

TiO_2 prepared from a mixture of rutile and anatase with <100 nm particle size was purchased from Sigma–Aldrich (Ref. 634662).

2.2. Instrumentation and operation method

All equipment was purchased from Sciware SL. The Multisyringe Flow Injection System is described in Fig. S1 (Supplementary Data), and included a multisyringe burette (BU4S; Crison Instrument SA) with programmable flow rates and equipped with three glass syringes (S1–S3, Salt-line series, Hamilton Bonaduz, Bonaduz, Switzerland). Each syringe was connected to a three-way solenoid head valve (V_1 – V_3 , N-Research, Caldwell, NJ, USA) allowing the connection of each syringe to either the flow network (ON, activated) or a solution or waste reservoir (OFF, deactivated). Two further solenoid 3-way valves (V_A and V_B) from Takasago Electric Inc. (Nagoya, Japan, type STV-3-N $\frac{1}{4}$ UKG) were used to accomplish the function of a sample injection loop (SL) in the flow network. They were powered by auxiliary supply ports of the multisyringe unit.

S_1 (5 mL) was used for sample aspiration and filling of the injection loop and was connected in OFF-position to waste. S_2 (5 mL) was filled with carrier being ultrapure H_2O and used to propel the prior loaded sample from the SL to a three-way confluence made of polymethyl methacrylate (PMMA). Here, it was mixed with the chromogenic reagent (see Section 2.1) expelled from S_3 (2.5 mL). Finally, it was pushed through a reaction coil (RC) and following the detection flow cell polytetrafluoroethylene (PTFE) tubes of 0.8 mm internal diameter (id) were used in the flow network. SL and RC were 40 cm and 50 cm long, corresponding to approximately 200 μ L and 250 μ L, respectively.

The detection system consisted of a white LED, a liquid waveguide capillary cell (LWCC-3100; World Precision Instruments,

Saratosa, FL, USA) with a 100 cm path length, and an USB2000 fiber optic spectrometer (Ocean Optics, Dunedin, FL, USA) connected to a computer via an USB interface. Both, the USB2000 spectrometer as well as the LED were mounted directly to the fiber optic ports of the LWCC using homemade adapters of PMMA. The LED was powered using a commercial mobile-phone charger and a 100 Ohm potentiometer connected in series.

The absorbances were measured at a wavelength of 450 nm and a reference wavelength was set at 600 nm where the analyte does not present any spectrophotometrical signal, allowing the compensation (subtraction) of unspecific light attenuation originated from refraction index changes or small air bubbles. All instrument controls and acquisition of spectrophotometric data were performed using the software package AutoAnalysis 5.0 (Sciware SL).

2.3. Sampling locations

Unfiltered seawater, surface sediments and *Posidonia oceanica* samples were collected in three different locations along the coast of Majorca Island (Spain) (Fig. 1). Two sampling sites were located at Palmira and Santa Ponça beaches (sampled on 20 and 21 of August 2011). The third was located at Ses Salines Cape (sampled on September 1st 2011), a pristine open area. Subsurface seawater of 1 m depth (SSW) and surface microlayer (SML, 100 μ m) were collected from a zodiac as prior described using a peristaltic pump (Tovar-Sánchez et al., 2010) and a glass plate (Stortini et al., 2012), respectively. At each station, 500 mL of seawater were collected into acid-cleaned LDPE bottles, following the clean protocol previously described for the analysis of trace metals (Bruland et al., 1979; Tovar-Sánchez, 2012). Surface sediments and *P. oceanica* leaves and rhizomes were collected at the same location as the water samples by scuba divers, stored in polyethylene bags, and frozen at $-20^\circ C$ until analysis.

2.4. Digestion method

For the digestion, the method proposed by Khosravi et al. (2012) was adapted to each sample matrix as described in the following:

2.4.1. Seawater

Samples were shaken vigorously and sonicated in ultrasonic bath during 15 min in order to disaggregate the TiO_2 particles and homogenate the sample. Then, 10 mL of sample were transferred into a porcelain crucible and dried at $70^\circ C$ until evaporation (approx 24 h). Then, 1 g of $K_2S_2O_8$ was added and the mixture was fused with a Bunsen burner during at least 10 min. The reaction was considered as completed when fuming ceased. Once cooled, the solid residue was completely dissolved by adding 10 mL of 0.1 M HNO_3 and stirring on a hot plate at approximately $90^\circ C$ during at least 5 min. Finally, the solution was filled up to 25 mL in a volumetric flask with 0.1 M HNO_3 and stored at $4^\circ C$ until analysis.

2.4.2. Sediments and macrophytes

The digestion of sediments and macrophytes was used for the first time with this reaction. Leaves and rhizomes of the macrophyte *P. oceanica* were separated and carefully rinsed with ultrapure water to remove fine sediments particles. Clean leaves and rhizomes of *P. oceanica* as well as sediment samples were dried at $60^\circ C$ during 24 h and milled in a pulverisette 6 (Fritsch GmbH, Idar – Oberstein, Germany) with a ZrO_2 bowl and 15 grinding balls (170 rpm during 10 min for the sediment samples and 250 rpm during 20 min for the *P. oceanica* samples) in order to obtain a fine dust of dry material. Approximately 0.1 g of sample was exactly weighed into porcelain crucible. Calcination in a Bunsen flame during at least 10 min was necessary for leaves and rhizomes prior the addition of 1 g of $K_2S_2O_8$ in order to obtain a white ashes. After the

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