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Abstract

An analytical method for the separation and determination of titanium dioxide nanoparticles in water samples has been developed. The separation was performed by Cloud Point Extraction (CPE) with Triton X-114. Titanium dioxide nanoparticles and ionic titanium were analysed in the surfactant rich phase and surfactant poor phase respectively, by inductively coupled plasma-mass spectrometry (ICP-MS). Parameters related to the CPE procedure such as Triton X-114 and NaCl concentrations were evaluated. Optimum concentrations of 0.03% (w/v) and 2.5 mM of Triton X-114 and NaCl respectively, were selected to develop this study. The TiO2 nanoparticles extracted were digested using HNO3 and H2O2 in an ultrasonic bath for 10 minutes at 60 ºC and analysed by ICP-MS. The analytical characteristics of the method (calibration, limits of detection and quantification, precision and recovery) were evaluated. The LOD and LOQ for Ti determination in the surfactant rich phase were 0.13 and 0.45 µg L-1, respectively. Finally, the method was applied for the determination of TiO2 nanoparticles in swimming pool water samples.

Keywords	TiO2 nanoparticles, Cloud Point Extraction (CPE), water, inductively coupled plasma mass spectrometry, Triton X-114.
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Highlights:

- Use of a simple and cheap separation technique, cloud point extraction, to separate ionic titanium and titanium dioxide nanoparticles
- The method used smaller amounts of reagents than other separation methods.
- The method was applied to the analysis of swimming pool water samples.

CLOUD POINT EXTRACTION AND ICP-MS FOR TITANIUM SPECIATION IN WATER SAMPLES

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Abstract

An analytical method for the separation and determination of titanium dioxide nanoparticles in water samples has been developed. The separation was performed by Cloud Point Extraction (CPE) with Triton X-114. Titanium dioxide nanoparticles and ionic titanium were analysed in the surfactant rich phase and surfactant poor phase respectively, by inductively coupled plasma-mass spectrometry (ICP-MS). Parameters related to the CPE procedure such as Triton X-114 and NaCl concentrations were evaluated. Optimum concentrations of 0.03% (w/v) and 2.5 mM of Triton X-114 and NaCl respectively, were selected to develop this study. The TiO_2 nanoparticles extracted were digested using HNO_3 and H_2O_2 in an ultrasonic bath for 10 minutes at 60 ºC and analysed by ICP-MS. The analytical characteristics of the method (calibration, limits of detection and quantification, precision and recovery) were evaluated. The LOD and LOQ for Ti determination in the surfactant rich phase were 0.13 and 0.45 μg L^{-1}, respectively. Finally, the method was applied for the determination of TiO_2 nanoparticles in swimming pool water samples.

Keywords

TiO_2 nanoparticles, Cloud Point Extraction (CPE), water, inductively coupled plasma mass spectrometry, Triton X-114.

1. Introduction

The applicability of nanosized materials has been increasing in the last few years due to their higher surface area and reactivity compared with their bulk form [1]. Metal-based engineered nanoparticle (ENPs) materials, such as Ag, TiO_2, CeO_2, ZnO, and Au have a widespread range of applications in research areas and industry. Titanium dioxide nanoparticles are widely used in the industry due to their variety of uses, such as in paints and varnishes, additive in many foods and personal care products. Due to its intensive use, TiO_2 nanoparticles are released into the environment allowing for potential health risks for humans and the eco-system. Titanium dioxide nanoparticles from sunscreens are released into the waters of swimming pools and could be accumulated due to the limited volume of the pools and the recirculation during the water treatment processes [2].

Several analytical techniques are reported in the literature for identification, characterisation and quantification of nanoparticles (NPs) in different matrix samples. Identification can be conducted by transmission electron microscopy (TEM) [3-5], scanning electron microscopy (SEM) [6] and dynamic light scattering (DLS) [4,5,7]. Quantification was performed after a separation step by using inductively coupled plasma mass spectrometry (ICP-MS) [4, 6, 7], inductively coupled plasma optical emission spectroscopy (ICP-OES) [7] and electrothermal atomic absorption spectroscopy (ETAAS) [8-10]. Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) has also been used in recent years for NP determination and characterisation. This technique gives information about the NP concentration as well as

the size distribution [11-15]. sp-ICP-MS is the technique that has mainly been used to discriminate titanium-containing nanoparticles and dissolved titanium in surface water and treated drinking water [12], river water samples [16], and recreational waters [14]. Fabricius et al. [4] compared five off-line fractionation procedures (dialysis, centrifugation, ultrafiltration, tangential flow filtration and cloud point extraction) for different nanomaterials (Ag, TiO_2, CeO_2, ZnO, and Au), and recommended ultrafiltration combined with microwave digestion previous to the ICP-MS measurements as the best general practice. Hollbrook et al.[17] used tangential flow filtration size fractionation combined with ICP-MS to quantify dissolved, microparticulate and particulate fraction of titanium in recreational swimming pools.

Because NPs are found in environmental samples at very low concentration levels, separation and preconcentration steps are necessary before their determination by ICP-OES, ETAAS or ICP-MS. Cloud Point Extraction (CPE) has been used in the past few years for the separation/preconcentration of organic compounds, metal ions and biospecies. Jing-Fu Liu et al. [3] reported in 2009, for the first time, a simple route for separation/preconcentration of various NMs previous to determination by UV-Vis spectroscopy. These authors also developed a preconcentration method based on the CPE technique with Triton X-114 for quantification and characterisation of traces of AgNPs in environmental waters [18]. Majedi et al. [19] evaluated a CPE approach for the preconcentration and quantification of trace CuO nanoparticles in environmental samples by GFAAS and ICP-MS. Speciation analysis of silver nanoparticles and ionic silver using cloud point extraction, followed by electrothermal atomic absorption spectrometry was carried out by López García et al. [20] and López-Mayán et al. [21]. Several non-ionic surfactants, such as Triton X-114, Triton X-100 or mixtures of both surfactants, PONPEs (polyoxyethylene-4-isononylphenoxyethers) have been used for

CPE procedures [21-23]. Triton X-114 is the most common surfactant used for the separation of inorganic NPs by CPE.

CPE presents certain advantages compared to other conventional techniques (liquid-liquid extraction), such as lower cost, smaller volumes of solvents and the possibility of using less toxic reagents [23]. The literature about the use of CPE for titanium nanoparticles preconcentration is scarce, with the exception of the first experiments by Liu et al.[3], and the studies of Fabricius et al.[4] and Yang et al.[24] using the conditions given by Chao et al.[25] and Hartmann et al. [10] respectively, for the speciation of silver nanoparticles and silver ions. Gavazov et al. [26] have recently written a review about the use of nanoparticles in CPE. Titanium dioxide nanoparticles can participate as carriers of Zn(II) into a rich surfactant phase of Triton X-114 [22]. After desorption with dithizone, Zn(II) can be determined colorimetrically. Different compounds (2',3,4',5,7 pentahydroxyflavone [27], Alizarin Red S and cetyltrimethylammonium bromide [28], 4-(2-pyridylazo) resorcinol [29]) were used to complex Ti(IV) previous to extraction with Triton X-114.

The development of simple methods of analysis is required to monitor the removal of TiO_2 nanoparticles from water, and the transformation of the dissolved and particulate species in the aquatic media. The aim of this research is to develop an analytical method to perform the separation of the two possible chemical forms of Ti in water samples(TiO_2 NPs and ionic Ti). For this, a simple extraction procedure to separate both Ti species using Triton X-114 as a surfactant agent was developed. ICP-MS was used for titanium determination in both phases (surfactant poor phase and surfactant rich phase) separated by the CPE procedure.

2. Materials and Methods

2.1 Chemicals and reagents

Ultrapure water of 18 MΩ cm obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA) was used throughout the work.

Sodium chloride 99.0% (Panreac Quimica, Barcelona, Spain) and Triton® X-114 (Sigma Aldrich, St. Louis MO, USA), were used for the CPE procedure. Titanium standard solution 1002±5 mgL^{-1} and glycerol for analysis were obtained from Merck (Darmstad, Germany). Yttrium standard for ICP, 1000 mg L^{-1}, Y_2O_3 in 2-5% HNO_3 (Panreac), scandium 1000 mgL^{-1} in 2% HNO_3 (Perkin Elmer, Waltham, MA, USA), and rhodium 1000 mg L^{-1} (Sigma Aldrich) were used as internal standards. TiO_2 nanoparticles <100 nm, rutile, 99.5%, were purchased from Sigma Aldrich. Hiperpur nitric acid 69% (w/v) and 33% (w/v) hydrogen peroxide were used for surfactant rich phase acid digestion and were purchased from Panreac (Barcelona, Spain).

To avoid contamination, all glassware and storage bottles were kept in 10% nitric acid for at least 48 h and rinsed three times with ultrapure water, dried and stored for their use.

2.2 Instrumentation

Titanium was determined using a NEXION 300X inductively coupled plasma mass spectrometer (PerkinElmer, Waltham, MA, USA) equipped with a quadrupole, a collision cell with helium (to minimize the presence of polyatomic interferences), and an autosampler ESI SCD 2X.

A Raypa 1 Model UCI-150 ultrasonic bath from Espinar S.L. (Barcelona, Spain), programmable for temperature ranging from 0 to 90ºC, and time up to 15 min, with a frequency of 35 kHz for the ultrasound energy and a total volume of 4 L, was used for

the CPE procedure. A Vortex Reax Top Vibrational shaker (Heidolph™, Schawaback, Germany) and laboratory angular analogical centrifuge Nihita model 2600 (maximum speed 4000 rpm) (Auxilab, Navarra, Spain) were also used.

2.3 Cloud Point Extraction procedure

An aliquot of 10 mL of water sample was introduced in a conical glass centrifuge tube and 300 µL of 1% (w/v) Triton X-114 and 125 µL of 0.2M NaCl were added. The mixture was homogenised and incubated at 40ºC for 30 min in a water bath and the tube was then centrifuged at 3500 rpm for 5 min. The supernatant was separated and used for ionic titanium determination by ICP-MS. The surfactant rich phase was acid digested for TiO_2 nanoparticle determination. Therefore, 250 µL of 69% HNO_3 and 125 µL 33% H_2O_2 were added to the surfactant rich phase and digested using an ultrasonic bath at 60ºC for 10 minutes. The digested fraction was then diluted with ultrapure water before analysis by ICP-MS. The scheme of the cloud point extraction procedure is shown in **Figure 1**.

2.4 Titanium determination by ICP-MS

Titanium was determined in the supernatant phase and in the acid digested surfactant rich phase by ICP-MS, using the instrumental conditions shown in Table 1. The surfactant poor phase (ionic Ti) was directly analysed. Two different calibration methods were used. Calibration using ionic titanium in NaCl, in a concentration ranging from 0 to 100 µg L^{-1} of Ti was used for ionic Ti determination in the supernatant phase. Calibration using TiO_2 nanoparticles and subjected to the CPE procedure (final concentration of Ti ranging from 0 to 60 µg L^{-1}) was used for TiO_2 nanoparticle determination in the acid digested surfactant rich phase.

3. Results and discussion

Experiments were carried out to select the optimum conditions for the extraction of TiO_2 nanoparticles by cloud point extraction. Preliminary experiments were based on previous studies reported in the literature [30]. Therefore, an aliquot of 7 mL of water sample spiked with TiO_2 NP concentration of 100 µg L^{-1} was introduced in a conical glass centrifuge tube and 500 µL of 1% (w/v) Triton X-114, 125 µL of 0.2 M NaCl were added and made up to 10 mL with ultrapure water. The mixture was homogenised and incubated at 40ºC for 30 min in a water bath and the tube was then centrifuged at 3500 rpm for 5 min. The supernatant was separated and used for ionic titanium determination by ICP-MS. In the first part of this study, TiO_2 recovery percentages in the surfactant rich phase were calculated taking into account the initial concentration and the Ti concentration remaining in the supernatant phase.

Before the CPE optimisation procedure, the stability of the TiO_2 nanoparticles suspension was evaluated. Therefore, initial suspensions of 200 mg L^{-1} of TiO_2 nanoparticles were prepared in 1% (w/v) Triton X-100 and in 1% (w/v) glycerol and sonicated for 1 minute before use. These solutions were diluted with ultrapure water to prepare NP suspensions at low concentrations. Aliquots of 7 mL TiO_2 NP suspension (100 µg L^{-1}) were subjected in triplicate to the CPE procedure described above and Ti was then determined in the supernatant phase by ICP-MS. The recovery percentages obtained were similar using glycerol and Triton X-114 to prepare the initial TiO_2 NP suspension. However, the reproducibility was better using 1%(w/v) glycerol and also the suspension remains stable during more time. Therefore, 1% (w/v) glycerol was selected to prepare the initial TiO_2 NP suspension (200 mg L^{-1}).

3.1 Optimisation of the CPE parameters

Parameters related to the CPE procedure such as concentrations of Triton X-114 and NaCl were evaluated. The first parameter studied was the Triton X-114 concentration. Therefore, the CPE procedure was applied, as mentioned before, to a 100 μg L^{-1} TiO_2 NP solution, using 130 μL of 0.2 M NaCl and volumes of 1% (w/v) Triton X-114 ranging from 100 to 700 μL (final concentration 0.01-0.07% (w/v)). Experiments were performed in triplicate for each level. The results obtained are shown in **Figure 2**. As can be seen in the figure, the recovery percentages (87-99%) increase with the amount of Triton X-114 until 0.03% (w/v) (recovery 99%) and then remain practically constant. Therefore, 0.03% (w/v) of Triton X-114 was selected in this study. This concentration is lower than that used by Yang et al. [24] (0.24 % (w/v)) for the determination of SiO_2 and TiO_2 in natural waters using CPE. The Triton X-114 concentration has a small influence in the TiO_2 NPs extraction. In any case, the concentration used in the present study (0.54 mM) is higher than the critical micelle concentration [3].

The influence of the NaCl concentration in the CPE procedure was also studied. Experiments were carried out using 0.03% (w/v) Triton X-114 and varying the volume of 0.2 M NaCl between 0 and 200 μL (final concentrations from 0 to 4 mM NaCl) in the CPE procedure. This experiment was applied in triplicate for each NaCl concentration. The results obtained (**Figure 3**) showed that the recovery percentages increase until a NaCl concentration of 2.5 mM and then remain practically constant. Therefore 2.5 mM NaCl was selected in this study.

Nanoparticles can be concentrated by CPE when the surface of those NPs is neutral [3, 22]. At higher pHs than the zero point charge (experimental range between 5.2-6.8 for TiO_2 [31]), the presence of sodium chloride increases the ionic strength, decreases the Coulomb repulsion between the NPs, improves phase separation, and enhances the

extraction efficiency [3]. This phenomena was reported previously in the literature [3,18].

3.2 TiO_2 NP determination in the surfactant rich phase

The next step in this study was the selection of the conditions for Ti determination in the surfactant rich phase. In the first experiment the surfactant rich phase was diluted with Milli-Q water and directly injected into the ICP-MS for Ti determination. The results obtained in this experiment showed poor repeatability and low recovery percentages. Taking into account previous studies reported in the literature [19, 30], acid digestion of the surfactant rich phase was carried out before titanium determination. The aim of sample digestion is the mineralisation of the surfactant rich phase to homogenise the sample and facilitate the introduction into the nebulisation system, improving the precision of the measurements. The ultrasound assisted digestion was selected due to the small volume of sample used, and to avoid dilution and subsequent preconcentration steps. Therefore, the surfactant rich phase was acid digested using 250 μL 69% HNO_3 and 125 μL 33% H_2O_2 in an ultrasonic bath at 60ºC for 10 minutes. The digested sample was then diluted with Milli-Q water before analysis by ICP-MS. The results obtained after this acid digestion showed an improvement in the repeatability (the RSD obtained was lower than 10%) and recovery of the method.

3.3 Analytical performance

Analytical performance was studied for Ti determination in the acid digested surfactant rich phase and also in the supernatant phase.

3.3.1 Calibration

Two different calibrations were compared for titanium determination in the supernatant phase. Aqueous calibration was prepared using an ionic Ti concentration range from 0 to 100 μg L^{-1}. A second calibration was prepared in the same range of concentrations, in a solution of 2.5 mM NaCl. This NaCl concentration was selected based on the concentration used in the CPE procedure, applied with the aim of simulating the matrix of the sample. The slopes as well as the correlation coefficients (r) obtained for both calibrations are shown in **Table 2**. Both calibrations showed good linearity, with correlation coefficients higher than 0.9980. The slopes of both calibrations were compared using the t test (95% significance level) [32], and statistical differences were observed. This meant that the matrix had influenced the sensitivity of the method; therefore, calibration prepared in 2.5 mM NaCl has been used for the determination of ionic titanium in the supernatant phase.

For Ti determination in the acid digested surfactant rich phase, a calibration curve prepared with TiO_2 nanoparticles (0-60 μg L^{-1} of Ti) in a pool of acid digested surfactant rich phase of blank samples was compared with a calibration with TiO_2 nanoparticles in the same range of concentrations, subjected to the CPE procedure. The results obtained (**Table 2**) showed statistical differences (95% significance level) between the slopes of both calibrations. Therefore, calibration subjected to the CPE procedure was used for titanium determination in the surfactant rich phase.

3.3.2 Sensitivity

The limit of detection (LOD) and limit of quantification (LOQ) for the method were calculated according to LOD=3SD/m and LOQ=10SD/m, where SD is the standard deviation of 11 measurements of a blank and m is the slope of the calibration graph.

LODs and LOQs obtained were 0.03 and 0.12 μg L^{-1}, respectively for Ti determination in the supernatant phase and 0.13 and 0.45 μg L^{-1}, respectively for Ti determination in the surfactant rich phase.

The limit of detection for Ti(IV) (0.03 μg L^{-1}) was lower than the value obtained (2.5 μg L^{-1}) by Mirzaei and Naeini [27] using morin (2',3,4',5,7 pentahydroxyflavone) as a complexing agent before CPE and quantification by FAAS. This method was applied to the analysis of well water, spiked water and a plant of Haloxylon. Kenawy et al. [28] complexed Ti(IV) with Alizarin Red S and cetyltrimethylammonium bromide at pH 3 before extraction with Triton X-114 using sodium sulfate to facilitate the separation of the phases at room temperature. The limits of detection obtained were 0.1 and 2.3 μg L^{-1} by ICP-OES and UV-Vis spectroscopy, respectively. The authors recommended the colorimetric method for Ti(IV) concentrations higher than 10 μg L^{-1}. These methods were applied to the analysis of water and geological samples. The detection limit of the method developed by Masrounia and Vaziry [29] using 4-(2-pyridylazo) resorcinol as complexing agent, was 5 μg L^{-1}, and it was applied to the analysis of river water and ores by UV-VIS.

The LOD obtained for the surfactant rich phase (0.13 μg L^{-1}, preconcentration factor: 10) in the present study is lower than the LOD obtained by Yan et al. [24] (1 μg L^{-1}), for Ti determination in the digested extract of TiO_2 nanoparticles obtained after applying a CPE procedure to environmental water samples previous to the determination by ICP-MS. In this case, a CPE procedure was carried out in a sodium acetate/acetic acid media, EDTA and using Triton X-114 as surfactant rich agent.

3.3.3 Selectivity

Experiments were performed to evaluate the capacity of the method to separate TiO_2 nanoparticles and ionic titanium. Therefore, solutions of 100 μg L^{-1} of Ti, as ionic titanium and TiO_2 nanoparticles were prepared and subjected to the CPE procedure. Titanium was determined in the acid digested surfactant rich phase by ICP-MS. The extraction efficiencies obtained were 9±2% and 98±2% for ionic titanium and TiO_2 nanoparticles, respectively. These results indicate that the method is selective for the extraction of TiO_2 nanoparticles and that ionic titanium remains in the supernatant phase.

3.3.4 Precision

The precision of the method was evaluated for TiO_2 nanoparticle determination by studying the repeatability (within-run precision) and the reproducibility. The repeatability was studied by analysing (10 times) the acid digested surfactant rich phase of a water sample. The reproducibility was studied using a water sample spiked with 100 μg L^{-1} of TiO_2 nanoparticles and subjected to the CPE procedure in quintuplicate. Relative standard deviations of 3 and 8% were obtained for the repeatability and reproducibility, respectively. Inter-day precision was also studied and RSDs lower than 10% were obtained.

In a previous study, Fabricius et al. [4] compared the precision of ICP-MS measurements in suspensions of TiO_2 NPs, obtaining RSDs of 3.2 % (MW-digested sample), 5.0% (acidified sample), and 13.3% (direct measurement). In the present study, the ultrasonic treatment was valid to obtain an acceptable precision compared to MW-digestion or acidification of the sample.

3.3.5 Recovery

Analytical recovery was assessed using a sample of swimming pool water spiked with 25, 50 and 100 μg L^{-1} of TiO_2 nanoparticles and subjected to the CPE procedure. Experiments were carried out in quintuplicate for each concentration level. Recovery percentages of 97±5 %, 104±8% and 102±7% were obtained for 25, 50 and 100 μg L^{-1} of TiO_2 NPs, respectively.

4. Determination of TiO_2 nanoparticles in water samples

The method was applied to the determination of ionic titanium and TiO_2 nanoparticles in three samples of swimming pool water. These samples were collected in summer in three different outdoor swimming pools where titanium NPs could be present, due to the use of health care products such as sunscreens.

The cloud point extraction procedure was performed in triplicate for all samples ,and both phases (surfactant poor phase and surfactant rich phase)were analysed in triplicate by ICP-MS. The results obtained are shown in **Table 3**. As can be observed, both species of titanium were detected and quantified in the samples analysed with titanium concentrations ranging from 3.5 to 5.0 μg L^{-1} as NPs, and from 2.5 to 8.3 μg L^{-1} in the ionic form.

The dissolved concentrations of titanium reported in the samples studied were slightly lower than those found by Hollbrok et al.[17] (41 ± 7.1 μg L^{-1}), and Venkatesan et al. [14] (5.42-18.2 μg L^{-1}) in recreational swimming pool waters. In the present study the percentage of dissolved titanium ranged from 41.6 to 66.4%, while Hollbrook et al. [17] observed that the major part of Ti was in the fraction < 1 kDa (82-92 %). Venkatesan et al. [14] used the background (baseline signal) obtained in the measurements by SP-ICP-MS to estimate the percentage of ionic titanium and particles smaller than the size detection limit (98.7–99.8%). These differences can be explained by the numerous

factors that can affect the concentration and the distribution of the species (density of bathers, pool volume, sampling time, irradiation, evaporation, water treatments, etc).

5. Conclusion

To the best of our knowledge this is the first method reported in the literature that allows for the separation of TiO_2 NPs and ionic Ti, using a cloud extraction procedure. TiO_2 NPs were extracted with Triton X-114, and the surfactant rich phase obtained was acid digested using ultrasonic energy and analysed by ICP-MS for Ti determination. The surfactant poor phase (ionic Ti) was directly analysed. The method showed a good selectivity for the separation of TiO_2 NPs in the presence of ionic titanium, sensitivity, precision and analytical recovery. The method was applied to the analysis of swimming pool water samples, and represents a new strategy to monitor the removal of TiO_2 nanoparticles from water and the concentration of the metallic species of the element. In the future, further studies will be performed to combine CPE and sp-ICP-MS.

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Table 1. Instrumental conditions for titanium determination by ICP-MS.

Component/Parameter	**Type/ Value/ Mode**
Nebuliser	PFA-ST Microflow nebuliser
Spray chamber	PC^3 Peltier Cooler-Quartz cyclonic
Triple cone interface material	Nickel/Aluminium
Plasma gas flow	18.0 L min^{-1}
Nebuliser gas flow	1.2 L min^{-1}
Sample uptake rate	0.94 L min^{-1}
RF power	1600 W
Integration time	50 ms
Replicates per sample	3
Operation mode	Standard
Isotopes	^{47}Ti, ^{48}Ti, ^{49}Ti
Internal standards (10 µg L^{-1})	^{45}Sc, ^{103}Rh, ^{89}Y

Table 2. Slopes and correlation coefficients for different calibration graphs.

Supernatant phase		
	Slope	**Correlation coefficient (r)**
Aqueous calibration	18797	0.9999
Calibration in 2.5 mM NaCl	13399	0.9982
Surfactant rich phase		
	Slope	**Correlation coefficient (r)**
Calibration prepared in acid digested surfactant rich phase of blank samples	17338	0.9980
Calibration subjected to the CPE procedure	7770.3	0.9993

Table 3. Results obtained for the analysis of titanium in samples of swimming pool water (n=3)

Sample	[Ti] µg L^{-1} NPs	[Ti] µg L^{-1} ionic
1	4.2±0.5	8.3±0.1
2	5.0±0.3	2.7±0.1
3	3.5±0.1	2.5±0.1

Figure captions

Figure 1. Cloud point extraction procedure

Figure 2. Influence of the Triton X-114 concentration in the extraction of TiO_2 nanoparticles (n=3).

Figure 3. Influence of the NaCl concentration in the extraction of TiO_2 nanoparticles (n=3).

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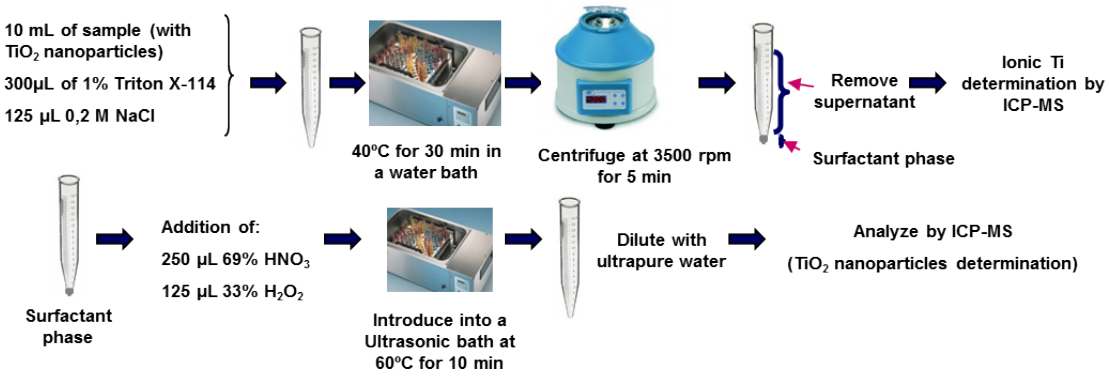
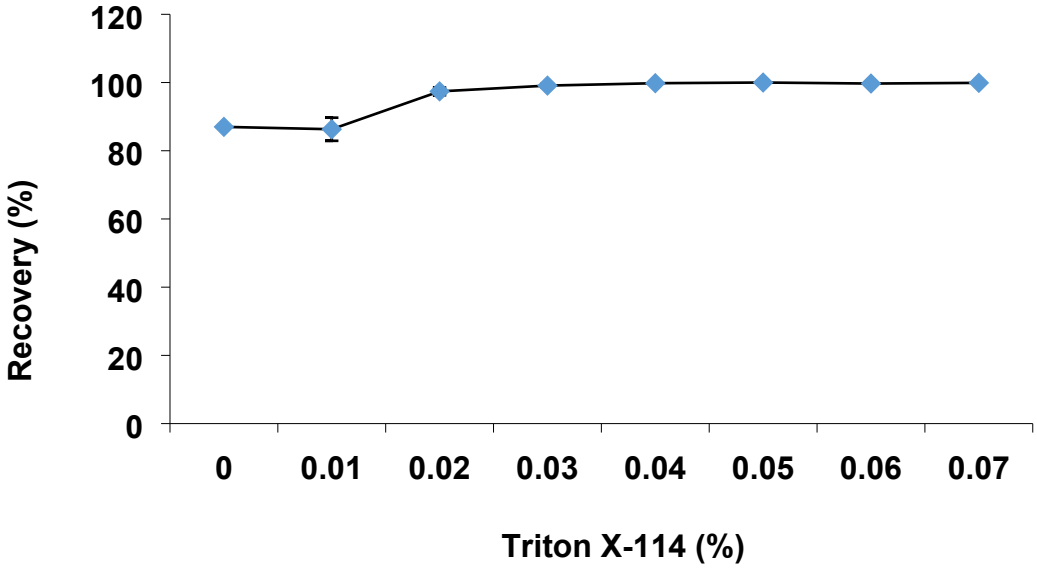
Figure captions

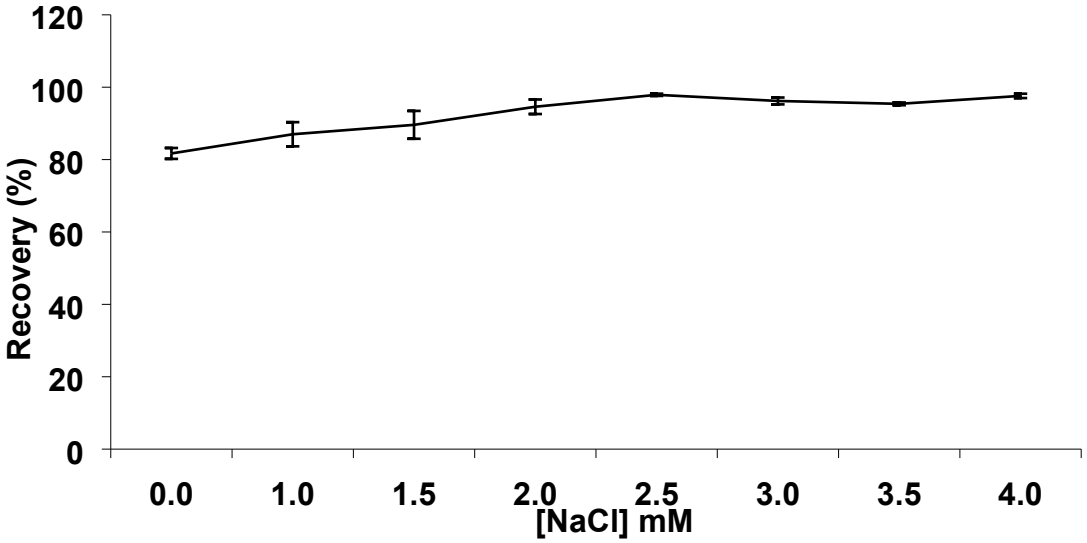
Figure 1. Cloud point extraction procedure

Figure 2. Influence of the Triton X-114 concentration in the extraction of TiO_2 nanoparticles (n=3).

Figure 3. Influence of the NaCl concentration in the extraction of TiO_2 nanoparticles (n=3).


10 mL of sample (with TiO_2 nanoparticles)
300µL of 1% Triton X-114
125 µL 0,2 M NaCl
40ºC for 30 min in a water bath
Centrifuge at 3500 rpm for 5 min
Remove supernatant
Surfactant phase
Ionic Ti determination by ICP-MS
Surfactant phase
Addition of:
250 µL 69% HNO_3
125 µL 33% H_2O_2
Introduce into a Ultrasonic bath at 60ºC for 10 min
Dilute with ultrapure water
Analyze by ICP-MS
(TiO_2 nanoparticles determination)


120
100
80
60
40
20
0
Recovery (%)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
Triton X-114 (%)


120
100
80
60
40
20
0
Recovery (%)
0.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
[NaCl] mM

Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: