



ORIGINAL ARTICLE

Solid-phase extraction of vanadium(V) from tea infusions and wines on immobilized nanometer titanium dioxide followed by ICP-OES analysis



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Abstract Nanosized titanium dioxide immobilized on silica gel was synthesized and used as fixed-bed phase for V(V) pre-concentration, followed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Three different sorbents were prepared by sol–gel method starting from a mixture of titanium isopropoxide, 2-propanol and water, and characterized by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and BET analysis. V(V), the most stable and toxic oxidation state of the element, present in water and beverages samples, was selectively sorbed, pre-concentrated, quantitatively eluted by 0.1 M HCl and analyzed by ICP-OES. The effectiveness of the procedure was first assessed on tap water enriched with $1 \mu\text{g L}^{-1}$ of V(V) obtaining recoveries up to 92% ($n = 4$). The pre-concentration step was then optimized for complex matrices such as tea infusions and red and white wines. The reliability of the procedure was assessed on the same beverages samples spiked with 20–250 $\mu\text{g L}^{-1}$. Quantitative recoveries (82–95%, $n = 4$) were assured avoiding any sample pre-treatment, generally essential in such complex matrices, obtaining good precision (RSD < 12%, $n = 3$). The method was then applied to the determination of V(V) in commercial tea infusions and wines.

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1. Introduction

Vanadium is a ubiquitous trace metal widely distributed in the environment. It exists in different oxidation states, the most common being V(IV) and V(V). The two oxidation states show different toxicity and the pentavalent form is the most toxic one (WHO, 2001). As a matter of fact, trace levels of vanadium are essential for normal cell growth, but higher concentration

can cause toxic effects. In particular, V(V) was shown to be a strong inhibitor of the enzyme Na and K-ATPase than V(IV) (Patel et al., 1990), and its high toxicity was proved in a study conducted on mice (Ma and Fu, 2009).

Foods represent the major source of exposure to vanadium for the general population (Barceloux, 1999; ATSDR, 2009). Actually it is normally present at concentration levels ranging from 1 to 5 $\mu\text{g kg}^{-1}$ in drinks and fruit juices (Filik and Aksu, 2012), from 4 to 41 $\mu\text{g L}^{-1}$ in tea infusions (Dundar and Saglam, 2004), and up to 90 $\mu\text{g L}^{-1}$ in wines (Teissèdre et al., 1998).

In view of these considerations, accurate analytical methods for the determination of vanadium in food matrices are required. Its determination usually requires a pre-concentration step due to both the low analyte concentration and the need to remove the matrix interferences. For this, the direct determination by the most common analytical techniques is a hard task. More expensive and sophisticated techniques, i.e. ICP-MS, suffer from strong interferences that can be overcome only using more expensive high resolution ICP-MS (Reed et al., 1994; Wang et al., 1999) or dynamic reaction cell (DRC) systems (Wang and Brindle, 2011). In the literature several procedures dealing with vanadium determination in food and beverages are reported, involving sample acidic digestion followed by elaborated pre-treatments, i.e. complexation, cloud point extraction, oxidation (Teissèdre et al., 1998; Dundar and Saglam, 2004; Shishehbore and Jokar, 2011; Filik and Aksu, 2012). Also solid-phase extraction (SPE), usually preferred to other techniques, is always applied after sample digestion and treatment with ligands (Wadhwa et al., 2013).

With regard to SPE, recent works investigated the adsorption behavior of metal ions on nanometer oxides such as CeO_2 (Vassileva et al., 1996; Vassileva and Furuta, 2001), Al_2O_3 (Chang et al., 2003) and TiO_2 (Liang et al., 2000). Due to their intrinsic surface reactivity, high surface area and high adsorption capacity, these nanocomposite materials have been used for separation and pre-concentration of metal ions in biological (Liang et al., 2001a,b) and environmental samples (Liu and Liang, 2007).

In this work, nanometer TiO_2 was prepared by a sol-gel method and immobilized on micrometric silica in order to dispose of a SPE adsorbent with good intrinsic surface reactivity and high surface area. The material was characterized and, for the first time, applied as a SPE sorbent for V(V) determination in untreated drinks. After pre-concentration, V(V) was analyzed by ICP-OES.

Sorbent phase, sample volume, adsorption capacity, eluent composition and volume, loading and elution flow rates have been accurately investigated. The procedure was then applied to analysis of commercial tea infusions, white and red wine samples.

2. Materials and methods

2.1. Chemicals and instruments

HCl 37%, $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, titanium (IV) tetraisopropoxide (97% v/v), 2-propanol (99.5% v/v) and vanadium stock solution 1.02 g L^{-1} were supplied from Sigma-Aldrich, NH_4VO_3 from Riedel-De Haën Ag Seelze-Hannover and silica 63 μm

from Merck. 200 mg L^{-1} V(V) standard solution was prepared by dissolving NH_4VO_3 in deionized water while V(IV) stock solution was prepared from $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ in 0.2 M HClO_4 . The exact vanadium concentrations of both solutions were determined by ICP-OES. Ultra-pure water (resistivity 18.2 $\text{M}\Omega \text{cm}^{-1}$ at 25 °C) was produced in laboratory by means of a Millipore Milli-Q system.

An ICP-OES Perkin Elmer Optima 3300 DV was used for all the measurements, following the operating conditions suggested by the manufacturer (plasma flow 15 L min^{-1} , aux flow 0.5 L min^{-1} , neb flow 0.85 L min^{-1} , RF power 1300 W, sample flow rate 1.5 mL min^{-1} , λ 292.402 nm). A four-point calibration curve, mean of three independent calibration lines, was generated in the concentration range 0.01–10.2 mg L^{-1} . Instrumental detection limit (IDL) and instrumental quantification limit (IQL) were calculated as 3 and 10 times the standard deviation related to the blank signal, respectively. IDL was 3 $\mu\text{g L}^{-1}$ and IQL was 10 $\mu\text{g L}^{-1}$.

A Shimadzu AA-6601G/GFA 6500 ET-AAS system was used for total vanadium determination (Teissèdre et al., 1998).

A Philips PW 1830 generator and a Cambridge S360 microscope were employed for XRPD and SEM analysis. ASAP 2010 physisorption analyzer (Micromeritics Instrument Corp) was used for BET and porosity analysis; samples were pre-treated at 200 °C in vacuum before measurement.

2.2. Synthesis of nanosized titanium dioxide immobilized on silica gel

Nanosized titanium dioxide immobilized on silica gel ($\text{TiO}_2/\text{SiO}_2$) has been prepared by sol-gel method (Caratto et al., 2012; Hench and West, 1990). In the first step, titanium isopropoxide, 2-propanol and ultrapure water were mixed under vigorous stirring for 4 h obtaining a white mellow gel. In the second step, silica gel was immersed in TiO_2 -precursor sol and mixed by magnetic stirring or sonication. The coated silica gel was washed two times with ultrapure water in order to remove dispersed TiO_2 . Finally the material was dried at 100 °C for 1 h and subsequently calcined at different temperatures in order to obtain crystalline anatase structure.

Three different samples were investigated in this study, ST1 = $\text{TiO}_2/\text{SiO}_2$ synthesized under magnetic stirring and calcined at 450 °C for 1 h; ST2 = $\text{TiO}_2/\text{SiO}_2$ synthesized under sonication and calcined at 450 °C for 1 h; ST3 = $\text{TiO}_2/\text{SiO}_2$ synthesized under magnetic stirring and calcined at 550 °C for 1 h.

2.3. Column preparation

Polypropylene columns (1.5–4 mL, Alltech, Italy) were filled with 0.05–1 g of nanosized TiO_2 immobilized on silica gel and conditioned to the native sample pH with 20 mL of 0.1 mol L^{-1} CH_3COONa buffer solution.

2.4. Sample preparation

For the optimization of the procedure, two types of wines (homemade white wine and Barbera from Oltrepò Pavese, Pavia) and a commercial no brand tea infusion (prepared by immersion of one tea bag in 200 mL of hot water for 5 min) were selected and analyzed with no further treatment. The

native total vanadium content was measured by atomic absorption spectroscopy with electrothermal atomization (ET-AAS) after acidic digestion (Teissèdre et al., 1998), and V(V) content was determined according to a validated method based on Chelex100 SPE followed by ICP-OES analysis (Sturini et al., 2010). Samples with no modification of the native pH were pre-concentrated (see Section 2.5); in detail, tea infusions and white wine were submitted to SPE as purchased, while red wine was 1:1 diluted.

2.5. Pre-concentration procedure

Samples (25 mL for wines, 50 mL for tea infusions) were delivered at 1 mL min⁻¹ flow rate throughout the columns. The pre-concentration system consisted of a multi-channel peristaltic pump (Gilson, Italy) equipped with a set of Tygon pump tubes to connect the samples with the columns. V(V) retained on the column (1 g sorbent) was quantitatively eluted by 0.1 M HCl solution (0.1 mL min⁻¹) and the effluent fractions were collected and analyzed by ICP-OES (3 × 1 mL for tea infusion, 2 × 1 mL for white wine and 5 × 1 mL for red wine).

3. Results and discussion

3.1. Characterization of nanosized titanium dioxide immobilized on silica gel

The obtained materials were characterized by X-ray powder diffraction (XRPD) technique, scanning electron microscopy (SEM) and BET analysis (Table 1). As shown in Fig. 1, all samples crystallized in anatase structure. It is well known that specific surface area of nanoparticles is related to their size, therefore three different procedures to immobilize nanosized titanium dioxide on silica gel were tested. Stirring and temperature of calcination affect the surface area; the larger one was observed on ST1 sample. The SEM analysis, reported in Fig. 2, showed that ST3 nanoparticles, calcined at 550 °C, were larger than ST1 and ST2, calcined at 450 °C. The grains of ST1 and ST2 maintained regular size and round in shape. Sample ST1 was more homogeneous than ST2 because the magnetic stirring is more controlled than sonication, and also than ST3 because its smaller anatase grains size allowed a more uniform coating.

3.2. Nanosized titanium dioxide immobilized on silica gel as SPE sorbent: explorative experiments

The affinity of V(IV) and V(V) for the three types of immobilized nanometer TiO₂, namely ST1, ST2, ST3, was investigated. 20 mL of V(IV) and V(V) aqueous solutions (1 mg L⁻¹) at different pHs was separately passed through the packed columns (0.05 g) following the procedure above described. For all the sorbents tested, a quantitative adsorption of V(V) (>95%) was observed in the pH range 2.3–7.0, while that of V(IV) was negligible (<5%) at acidic pHs; note that vanadyl cation is stable only at pH < 2.4 because of its easy oxidation to vanadate by dissolved oxygen (Sturini et al., 2010). In the pH range 2.5–7 VO₂⁺ and H₂VO₄⁻/HVO₄²⁻ are the prevalent species of vanadium(V) (Pyrzynska and Wierzbicki, 2004); being the sorbent point of zero charge

Table 1 Surface areas obtained by BET analysis on ST1, ST2 and ST3. Single point surface areas have been calculated using $P/P_0 = 0.30196$.

Sample	Surface area (m ² g ⁻¹)	Single point surface area (m ² g ⁻¹)
ST1	355.91	347.97
ST2	299.68	290.69
ST3	226.34	225.73

(PZC) 5.9 ± 0.1 , electrostatic interactions play an important role in the adsorption process.

The V(V) pre-concentration procedure was first developed in tap water samples enriched with 250 µg L⁻¹ V(V), and eluent composition and volume, loading and elution flow rates were investigated.

For elution of V(V), aqueous HCl, HNO₃, NaOH and NH₃ at different concentrations (0.1–1 M) were tested. 0.1 M HCl resulted the best eluting solvent, providing a quantitative desorption of vanadium (95%, $n = 3$) with no interferences in the ICP-OES analysis, while recoveries not higher than 60% were obtained employing either different concentrations or elution solvents. The optimum elution volume was found by collecting and analyzing fractions of 1 mL; 3 × 1 mL eluting solutions were sufficient to entirely elute the analyte from ST1 and ST2, providing at the same time suitable enrichment factors for analytical application. On the contrary, even using higher HCl concentration (1 M) and/or larger elution volumes (up to 8 mL) a recovery not higher than 60% ($n = 3$, RSD 5%) was found on ST3.

Since the loading flow rate (0.1–2 mL min⁻¹) did not affect the pre-concentration efficiency (data not shown), for practical reasons it was performed at 1 mL min⁻¹. Contrariwise, the elution flow rate significantly affected recovery. Decreasing the flow rate from 1 to 0.1 mL min⁻¹, recovery gradually increased up to 96% (RSD 5%, $n = 3$) due to a more efficient desorption of the adsorbed analyte.

On the basis of the analytical features above reported and of the SEM, XRPD and BET characterizations, ST1 was preferred for V(V) pre-concentration.

3.3. Analytical evaluation of the method

A series of experiments were first performed to evaluate the V(V) pre-concentration efficiency of ST1 from tap water and from more complex matrices (i.e. wines and tea infusion), and to characterize the main figures of merit of the proposed method.

In order to evaluate the maximum applicable sample volume, 20, 50, 100, and 250 mL of aqueous solutions containing 10 µg of V(V) were loaded on the column (0.05 g ST1) under the conditions above reported. A quantitative retention of V(V) was observed up to 70 mL. 25 mL of solutions at different V(V) concentrations (3–60 mg L⁻¹) was processed on ST1 to determine the adsorption capacity that was found to be 11 mg g⁻¹. The column was proved to be reusable, after reconditioning at sample pH, for at least 10 adsorption-elution cycles, with no significative decrease in the recovery of V(V) ($p = 0.05$).

To test recovery and precision of the proposed pre-concentration procedure at lower concentrations, additional experiments were carried out on tap water spiked with 1 µg L⁻¹ V(V), obtaining quantitative recovery rates, with mean values up to 92% (see Table 2).

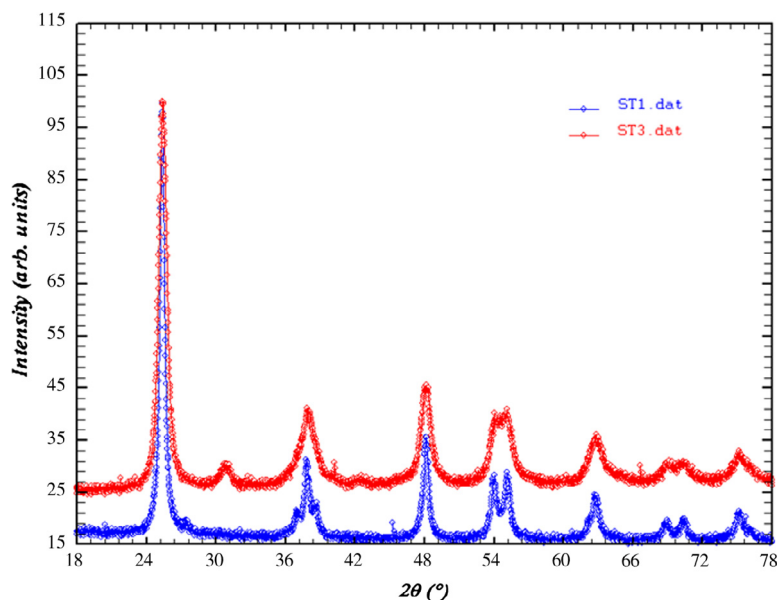


Figure 1 XRPD spectra of samples ST1 (blue) and ST3 (red) showing crystalline anatase phase. The spectra of ST1 and ST2 are overlapped because of the same temperature and time of calcination.

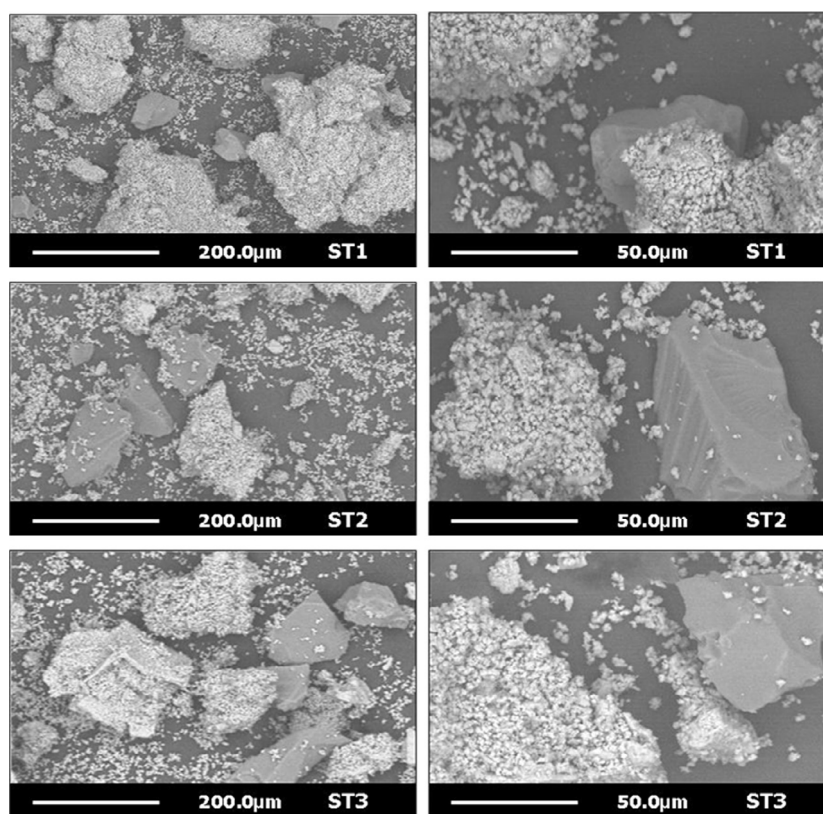


Figure 2 SEM images (dimension: 50–200 μm , magnification: 5000–100, EHT: 20.0 kV). Top: cluster of ST1. Middle: cluster of ST2. Bottom: cluster of ST3.

With the aim of developing a straightforward procedure for the determination of V(V) in beverages, further experiments were devoted to evaluate the efficiency of the ST1 sorbent phase in the pre-concentration of V(V) from more complex matrices. A commercial tea infusion and two wine samples were analyzed for vanadium(V) and total vanadium content

by two independent validated methods (Chelex 100 SPE-ICP-OES and ET-AAS, respectively, see Section 2.4), and the measured amounts are included in Table 2.

In the absence of a certified reference material for V(V), the accuracy was tested by recovery tests on the same samples enriched with known amounts of V(V), as reported in Table 2.

Table 2 Analytical figures of merit obtained for V(V) determination by the proposed SPE-ICP-OES procedure.

Sample	Total native V ^a ($\mu\text{g L}^{-1}$)	Native V(V) ^b ($\mu\text{g L}^{-1}$)	V(V) added ($\mu\text{g L}^{-1}$)	V(V) found ($\mu\text{g L}^{-1}$)	Recovery%	Intraday precision (RSD%, $n = 4$)	Interday precision (RSD%, $n = 3$)	Enrichment factor	MDL ^c ($\mu\text{g L}^{-1}$)	MQL ^d ($\mu\text{g L}^{-1}$)
Tap water	< 1	< 0.3	1	0.92	92	7.6	9.5	23	0.1	0.4
Tea infusion	< 1	< 0.4	20	16.8	84	7.1	10.1	17	0.2	0.6
			100	82	82	9.8	–	–	–	–
			250	220	88	11.4	–	–	–	–
White wine	12	11	20	28	90	5.6	9.8	12.5	0.2	0.8
			100	105	95	8.4	–	–	–	–
			250	235	90	4.4	–	–	–	–
Red wine	20	21	20	36	88	7.9	11.7	5	0.6	2.0
			100	103	85	9.4	–	–	–	–
			250	233	86	10.5	–	–	–	–

^a Determined by ET-AAS after acidic digestion (Teissèdre et al., 1998).

^b determined by Chelex100 SPE followed by ICP-OES analysis (Sturini et al., 2010).

^c MDL, method detection limit.

^d MQL, method quantification limit.

Table 3 Chemical composition of tea infusion and wine samples: cations and anions. RSD 1.1–2.2% ($n = 3$).

	Tea infusion	Homemade wine (white wine)	Barbera (red wine)
pH	5	2.8	3.1
Sodium (mg L^{-1})	1	16.5	39
Potassium (mg L^{-1})	51	419	657
Calcium (mg L^{-1})	1.7	60	85
Magnesium (mg L^{-1})	3.4	52	65
Zinc (mg L^{-1})	0.9	0.7	0.9
Iron (mg L^{-1})	0.04	6	2.8
Manganese (mg L^{-1})	1.3	0.4	1.0
Chloride (mg L^{-1})	15.4	15.6	44.8
Nitrate (mg L^{-1})	1.8	4.2	16.7
Sulfate (mg L^{-1})	24.3	178	305
Phosphate (mg L^{-1})	22.4	735	690

Working in the conditions above reported (0.05 g ST1, loading flow rate 1 mL min^{-1} , elution flow rate 0.1 mL min^{-1} , sample volume 25 mL) the recovery obtained by processing tea infusion and wine samples enriched with $250 \mu\text{g L}^{-1}$ V(V), did not exceed 25%. This was due to the partial adsorption of the metal ion on the sorbent phase, as proved by the consistent analyte amounts found in the percolated samples. These findings suggested that two different processes could have hindered V(V) adsorption, namely competition between the metal ion and the matrix constituents for the sorption sites, and/or the formation of stable complexes between V(V) and the organic species present in wine and tea.

To understand the reasons at the basis of these hypotheses, 50 mL of tea infusion with a negligible vanadium content ($< 1 \mu\text{g L}^{-1}$) was passed through the column followed by 5 mL of an aqueous solution containing V(V) ($250 \mu\text{g L}^{-1}$). In this case, the V(V) not retained was 58%, proving that a competition between the metal ion and the matrix constituents effectively took place. A similar behavior was found for red and white wines. To improve V(V) adsorption from such complex matrices, the sorbent amount was varied from 0.05 to 1.0 g. SPE of 25–50 mL samples spiked with $250 \mu\text{g L}^{-1}$ V(V) was performed. Sample volumes of 25 and 50 mL for wines

and tea infusions, respectively, provided recoveries up to 98% ($n = 3$, RSD 5%). The elution was carried out with different volumes of 0.1 M HCl depending on the matrix, that is $3 \times 1 \text{ mL}$ for tea, $2 \times 1 \text{ mL}$ for white wine and $5 \times 1 \text{ mL}$ for red wine. Under these conditions, tea infusion and wine samples spiked at concentrations near to those found in such beverages (Teissèdre et al., 1998) were pre-concentrated obtaining good recovery and intraday precision, as reported in Table 2. The within-laboratory inter-day precision, evaluated on three samples of each beverage independently spiked at the lowest concentration levels and pre-concentrated in different days, provided RSDs $< 12\%$. The method detection and quantification limits (MDLs, MQLs, respectively), reported in Table 2, prove that the proposed procedure is suitable for the determination of V(V) at the concentration levels usually present in actual beverages (Teissèdre et al., 1998).

As it is evident, enrichment factor depends on the sample type. In particular, for such complex matrices rich in polyphenols, flavonoids, organic acids, non-volatile alcohols, sugars, metal ions, anions (Grindlay et al., 2011), the loading volume is obviously lower than that applicable for water. The major coexisting cations and anions present in the actual beverages were measured and reported in Table 3. It can be seen that the presence of these coexisting ions has no influence on the V(V) recovery under the selected conditions (see Table 2). The SPE procedure on nanometer $\text{TiO}_2/\text{SiO}_2$ allowed at the same time to perform a cleanup of the sample, thus permitting the final quantification of the analyte in the eluate, with no need for sample pretreatment (e.g. acidic digestion followed by V(V) complexation) prior the pre-concentration step.

To evaluate the potential matrix effect on the ICP-OES measurement, the matrix-matched calibration was also performed. Three independent four point calibration curves were generated in the range $20\text{--}500 \mu\text{g L}^{-1}$ by analysis both in HNO_3 (0.5%, v/v) aqueous solution (external calibration) and in the SPE eluates of each beverage. The matrix-effect was evaluated by comparing the respective slopes observed in HNO_3 (0.5%, v/v) aqueous solution and in matrix-matched solution. The slope values resulted not significantly different ($p = 0.05$), indicating that the matrix effect was negligible. Good linearity was observed, with correlations coefficients (r) higher than 0.9998.

3.4. Application to commercial beverages

The TiO₂/SiO₂-based SPE procedure was applied for determining V(V) in commercial Italian wines (Ortrugo, 11% vol. and Merlot, 12% vol.) and two tea infusions (Earl Grey and Green Blends). V(V) was effectively determined in the commercial wines at concentration levels of some tens of micrograms *per* liter, namely 26 µg L⁻¹ in Merlot and 80 µg L⁻¹ in Ortrugo (RSD < 5%, *n* = 3). Differently, V(V) concentration was below MDL in the two tea infusions.

To further assess the reliability of the procedure, four independent aliquots of each sample were spiked with 0, 50, 100 and 250 µg L⁻¹ V(V), pre-concentrated on the ST1 sorbent, and then analyzed. Results obtained by the standard addition method were in excellent accordance with those found by external calibration (differences < 4%), substantiating the quantitative recovery of the metal ion also from these complex matrices. This further gave evidence of the good overall accuracy of the SPE-ICP-OES procedure here presented.

4. Conclusions

A simple procedure for direct V(V) determination in drinking waters and beverages has been developed. The pre-concentration makes use of an inexpensive and easy to be prepared solid-phase extraction adsorbent consisting of nanometer TiO₂ supported on silica microparticles. This proved to be suitable for analytical application combining sample cleanup and quantitative determination of the analyte. Good accuracy was obtained in water samples and also in more complex matrices, i.e. wine and tea, with no sample pre-treatment. The satisfactory analytical features and the practical advantages of the proposed method make it a reliable alternative to the more working procedures currently reported in the literature.

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