

Scientific paper

# Analytical Application of Nano-Sized Titanium Dioxide for the Determination of Trace Inorganic Antimony in Natural Waters

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## Abstract

In this work, solid phase extraction (SPE) using nano-sized TiO<sub>2</sub> as a solid sorbent was used for separation/preconcentration of total inorganic antimony (iSb) before its determination by electrothermal atomic absorption spectrometry (ETAAS). After adsorption of iSb onto nano-sized TiO<sub>2</sub>, direct TiO<sub>2</sub>-slurry sampling was used for sample injection into a graphite tube. The conditions for the reliable slurry sampling together with careful control of the temperature program for the slurry solutions were worked out. Extraction conditions for both inorganic antimony species (Sb(III) and Sb(V)) and interference studies of coexisting ions were studied in detail. The accuracy of the optimized method was checked by the certified reference material (CRM) for trace elements in lake water TMDA-61. Finally, the optimized method was used for the determination of trace inorganic antimony in synthetic and natural waters.

**Keywords:** Inorganic antimony, solid phase extraction, nano-sized TiO<sub>2</sub>, slurry sampling ETAAS

## 1. Introduction

In natural waters antimony mainly occurs at (ultra)trace levels in two inorganic forms as antimonate Sb(V) and antimonite Sb(III).<sup>1–3</sup> Determination of (ultra)trace concentrations of these inorganic forms requires reliable procedures for their separation and preconcentration to improve selectivity and sensitivity of the used detection method.

Most of the analytical procedures for the separation/preconcentration of antimony in waters is based on the coupling of high-performance liquid chromatography (HPLC) to hydride generation atomic absorption spectrometry (HGAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or inductively coupled plasma mass spectrometry (ICP-MS).<sup>4–9</sup> However, methods above mentioned are time consuming and require high operation costs. Thus, a simple and efficient separation/preconcentration technique in combination with a widely used detection method such as electrothermal atomic absorption spectrometry (ETAAS) can be more essential for using in common labs.

Among the separation/preconcentration techniques, solid phase extraction (SPE) has become the most frequently used for (ultra)trace metal analysis.<sup>10–13</sup> SPE techniques can be used in two modes as column or batch technique. In both techniques, analytes are sorbed on different materials and eluted with a small volume of suitable reagents. Then, the separated and preconcentrated analytes are determined in the elution solution by an appropriate analytical method. Since the elution is time-consuming and sometimes results in a loss of the analytes, direct slurry sampling of the used sorbent with the sorbed analytes is an effective mode to solve this problem.

In recent years, different nano-sized inorganic oxides (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, ZnO) have been used as solid sorbents due to their special physical and chemical properties such as high adsorption capacity, great adsorption speed, and low temperature modification.<sup>11,13</sup> Among them, increased attention in the field of (ultra)trace metal analysis is put on nano-sized TiO<sub>2</sub> which offers a high surface area/body weight ratio, high chemical stability and insolubility in acidic and alkaline solutions.<sup>14–30</sup> The point

of zero charge (PZC) for TiO<sub>2</sub> (anatase form) is located in the middle of the pH scale ( $6.8 \pm 0.2$ ), which enables to study adsorption events on both positively and negatively charged TiO<sub>2</sub> surfaces over a broad range of pH and ionic strength.<sup>31,32</sup>

In this study, a combination of batch experiments using nano-sized TiO<sub>2</sub> (as a solid sorbent for the separation/preconcentration of total iSb) and direct slurry sampling ETAAS (for the determination of antimony after its adsorption onto nano-sized TiO<sub>2</sub>) was used. This combination is much more convenient and it has provided good analytical results with some advantages over conventional procedures (already mentioned; diminishing the turnaround time and operational work; minimization of analyte losses caused by the incomplete release of the analyte from the used sorbent). However, the slurry analysis is not completely free of drawbacks. The most critical factor is the need for maintaining the stability of the slurry until sample injection.<sup>33</sup> In the case of TiO<sub>2</sub>-slurry sampling, the change of the quality of the graphite surface of the used tube is another drawback of the combination.<sup>34</sup> In spite of the drawbacks, combination of the optimized SPE using nano-sized TiO<sub>2</sub> as a solid sorbent and direct TiO<sub>2</sub>-slurry sampling ETAAS (after adsorption of iSb onto TiO<sub>2</sub>) provides reliable analytical results. The possibility of direct slurry injection into a graphite tube is the main advantage of ETAAS.

The aim of the present work was to propose, optimize and use a relatively simple SPE method for separation/preconcentration of total iSb in combination with ETAAS determination of the analyte. Careful control of the temperature program for the slurry solutions together with extraction conditions for both inorganic antimony species (Sb(III) and Sb(V)), and interference studies of coexisting ions were done. After optimization, a certified reference material (CRM) for trace elements in lake water TMDA-61 was used for checking the accuracy of the method. Finally, the optimized method was applied for the trace determination of iSb in synthetic and natural waters.

## 2. Experimental

### 2.1. Apparatus

All measurements were carried out with a Perkin-Elmer 3030 atomic absorption spectrometer (Überlingen, Germany) equipped with an HGA 600 graphite furnace. The spectrometer was provided with a Zeeman-based background corrector. All the measurements were performed in the peak area mode. Pyrolytic graphite tubes (Perkin-Elmer) were used exclusively. Atomization from the wall of the graphite tubes was performed. Argon was used as the purge gas. The hollow cathode lamp for Sb (Perkin-Elmer) was operated at 20 mA with a spectral bandwidth of 0.7 nm. The selected wavelength was 217.6 nm. Injection of a sample solution (20 µL) was followed by modifier so-

lution (10 µL of palladium nitrate). The temperature program is shown in Table 1.

For the determination of the adsorption capacity of TiO<sub>2</sub> (concentration of model solutions in the range of 0.1–50 mg L<sup>-1</sup>) ICP-OES (Jobin Yvon Model 70 Plus sequential spectrometer (Longjumeau, France)) was utilized. Optimal operation conditions were as follows: RF power 1000 W, outer Ar flow rate 12.0 L min<sup>-1</sup>, sheath Ar flow rate 0.15 L min<sup>-1</sup>, carrier Ar flow rate 0.35 L min<sup>-1</sup>, sample flow rate 1.0 mL min<sup>-1</sup>, wavelength 206.833 nm, entrance slit 20 µm, and exit slit 25 µm.

For the determination of antimony by HGAAS, a Perkin Elmer 1100 B atomic absorption spectrometer (Überlingen, Germany) equipped with continuous hydride system HG-2 (Labtech, Czech republic) was used. Samples in media of hydrochloric acid (1.5 mol L<sup>-1</sup>) reacted with a solution of 1% (m/v) sodium tetrahydroborate stabilized in 1% (m/v) sodium hydroxide. The gaseous products were separated from the solution (in the liquid-gas separator) and swept by a stream of argon (flow rate 300 mL min<sup>-1</sup>) to an electrically heated quartz tube (900 °C) mounted in the light path of an electrodeless discharge lamp for antimony (power 10 W). A spectral band pass of 0.7 nm was selected to isolate the 217.6 nm line. The stabilization time was 60 s.

In the extraction procedure an ionometer MS-31 (Praque, Czech republic) equipped with a glass-combination electrode, an analytical balance Sartorius 1702 (Göttingen, Germany), a mechanical shaker LT2 (Kavaler, Sazava, Czech Republic), and a centrifuge MPW-360 (Mechanika precyzyjna, Warsaw, Poland) were used.

**Table 1.** Temperature program for the determination of antimony by ETAAS.

Stage	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min <sup>-1</sup> )
Drying	110	20	30	250
Pyrolysis	1200	20	30	250
Atomization	2500	0	4	0
Cleaning	2600	1	3	250

### 2.2. Reagents and Samples

All reagents were of analytical grade and all solutions were prepared in doubly deionized water (DDW). Titanium dioxide (anatase form, nanopowder, < 25 nm, 99.7%; Sigma-Aldrich, Steinheim, Germany) was used as a sorbent for SPE. Stock standard Sb(III) and Sb(V) solutions (1000 mg L<sup>-1</sup>) were prepared by dissolving appropriate amounts of potassium antimony tartrate (Sigma-Aldrich) and potassium hexahydroxyantimonate (Sigma-Aldrich) in DDW, respectively. Model antimony solutions were prepared by stepwise dilution of the stock solutions

in DDW just before use. Calibration antimony solutions ( $10\text{--}80\ \mu\text{g L}^{-1}$ ) were prepared by stepwise dilution of the stock antimony standard solution ( $1003 \pm 2\ \text{mg L}^{-1}$  of Sb) (Merck, Darmstadt, Germany) in  $0.2\%$  (v/v)  $\text{HNO}_3$  also before use. Nitric acid (Merck) and sodium hydroxide (Merck) were employed to adjust the final pH of the model solutions and samples. Tetrahydroborate, potassium iodide, and hydrochloric acid (all Merck) were used for the determination of Sb by HGAAS. All glassware was kept in  $10\%$  (v/v) nitric acid (Lachema, Brno, Czech Republic) for at least 24 h and washed three times with DDW before use. A chemical modifier solution was prepared by diluting palladium nitrate stock solution ( $10\ \text{g L}^{-1}$  of Pd) (Merck) in DDW. Solutions with studied concentrations of potentially interfering elements were prepared by stepwise dilution of their stock solutions ( $1000\ \text{mg L}^{-1}$ ; all Merck) in DDW just before use.

Five types of synthetic fresh waters (SFWs) were produced following Weber<sup>35</sup> which varied in chemical composition defined by their relative hardness (i.e., very soft to very hard). In the case of these five water types, hardness and alkalinity were directly proportional. Chemicals ( $\text{NaHCO}_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSO}_4$ , and  $\text{KCl}$ ; all Merck) were added to DDW to produce very soft water (VSW), soft water (SW), moderately hard water (MHW), hard water (HW), and very hard water (VHW) as indicated in Table 2. Natural mineral waters (NMWs) from different parts of Slovakia (NMW1 from Mostova; NMW2 from Plesivec; NMW3 from Brzotin; NMW4 from Roznava) and natural creek water (NCW) from creek near mine dump in Pezinok were used as real samples for the determination of trace inorganic antimony (iSb).

All water samples were stored in an insulated cooler and delivered on the same sampling day to the laboratory for the analysis of iSb. In the laboratory, the samples were filtered through  $0.45\ \mu\text{m}$  pore size membrane filters and used for SPE.

Certified reference material (CRM) for trace elements in lake water TMDA-61 (National Water Research Institute, Burlington, Canada) were used for checking the accuracy of the optimized method.

fied with  $\text{HNO}_3$  ( $\text{pH } 2.0 \pm 0.1$ ) were placed into a 100 mL  $\text{HNO}_3$ -washed high-density polyethylene (HDPE) bottle containing 50 mg of nano-sized  $\text{TiO}_2$ . The sample solution was shaken by a mechanical shaker at laboratory temperature for 10 min. Then, the mixture was centrifuged at 4000 rpm for 10 min and the bulk aqueous phase was easily decanted by simply inverting the bottle. Finally, 5 mL of DDW was added to prepare a slurry sample (pH of the slurry was  $2.5 \pm 0.2$ ). The slurry sample was shaken by a mechanical shaker at laboratory temperature for 10 min. Before injection of the slurry solution into a graphite tube, the slurry was agitated again (1 min) and transferred into an autosampler cup.

For PF 20 and 30, aliquots of 80 and 90 mL of an acidified sample solution were placed into a 100 mL HDPE bottle containing 40 and 30 mg of nano-sized  $\text{TiO}_2$ , respectively. Then, the optimized SPE procedure described above was applied. Finally, 4 and 3 mL of DDW, respectively, was added to prepare a slurry sample.

The described procedures were repeated four times for model and sample solutions and ten times for CRM of lake water (TMDA-61) and blank solution.

Finally, the preconcentrated antimony in the samples was determined by ETAAS according to the furnace conditions listed in Table 1.

## 3. Results and Discussion

### 3.1. Optimization of the Furnace Conditions

Reliable determination of antimony by ETAAS is impossible without a chemical modification. It is caused by difficulties related to the loss of volatile compounds of this analyte at relatively low temperatures.<sup>36</sup> Many different chemical modifiers were proposed and utilized for the thermal stabilization of antimony in ETAAS determination. Most widely used are compounds of platinum group metals (PGMs), primarily palladium ones.<sup>37–40</sup> To establish a suitable temperature program for antimony determination in liquid and slurry solutions in this work, pyrolysis and atomization curves in the presence of palla-

**Table 2.** Five types of synthetic fresh waters and their actual initial pH.

Synthetic fresh water (SFW)	Amount of each chemical added to DDW ( $\text{mg L}^{-1}$ )				Actual initial pH
	$\text{NaHCO}_3$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{MgSO}_4$	$\text{KCl}$	
Very soft water (VSW)	12.0	7.5	7.5	0.5	6.57
Soft water (SW)	48.0	30.0	30.0	2.0	7.67
Moderately hard water (MHW)	96.0	60.0	60.0	4.0	7.96
Hard water (HW)	192.0	120.0	120.0	8.0	8.31
Very hard water (VHW)	384.0	240.0	240.0	16.0	8.36

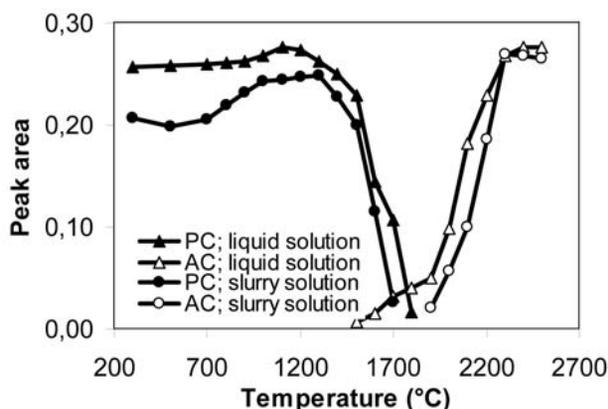
### 2.3. Extraction Procedure

For the optimized SPE with preconcentration factor 10 (PF 10), aliquots of 50 mL of a sample solution acidi-

dium nitrate ( $1.0\ \text{g L}^{-1}$  of Pd) were obtained. The pyrolysis and atomization temperatures were investigated in the range of  $300\text{--}1800\ ^\circ\text{C}$  and  $1500\text{--}2500\ ^\circ\text{C}$ , respectively

(see Fig. 1). The analysis of the TiO<sub>2</sub>-slurry sample resulted in a maximum loss-free pyrolysis temperature of 1300 °C; the analysis of the liquid standard solution resulted in a maximum loss-free pyrolysis temperature of 1200 °C. The absorbance reached the maximum increasing the atomization temperature to 2400 °C in both cases. Based on the observations described above, a pyrolysis temperature of 1200 °C and atomization temperature of 2500 °C were selected and used in subsequent experiments (see Table 1).

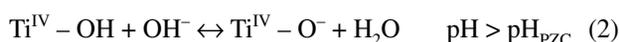
After injection of TiO<sub>2</sub>-slurry, the change of the quality of the graphite surface of the used tube is observed after a few atomization cycles. While peak area is not affected by the change, peak height is affected dramatically. Using peak area for evaluation, reproducible results can be achieved till the end of the lifetime of the used tube (around 200 firings).



**Figure 1.** Pyrolysis curves (PC) and atomization curves (AC) for antimony solutions (measured in the presence of palladium nitrate; injection volume of the modifier: 10 µL; concentration of palladium: 1.0 g L<sup>-1</sup>).

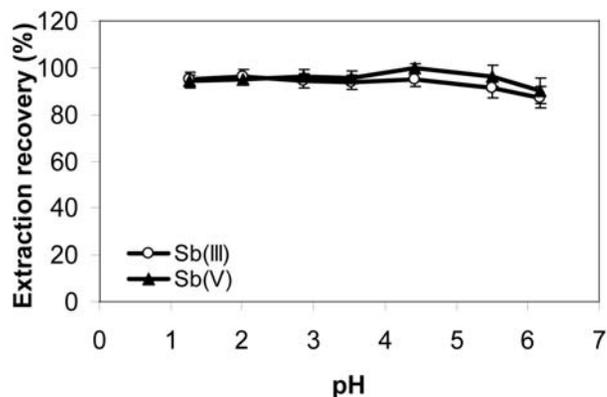
### 3. 2. Optimization of the Analytical Procedure

The first critical parameter evaluated for its effect on the extraction recovery of both inorganic antimony species (Sb(III) and Sb(V)) was the pH. In water solutions, the surface of TiO<sub>2</sub> can be positively or negatively charged, according to eqs 1 and 2.<sup>23,25,41</sup> The point of zero charge (PZC) of TiO<sub>2</sub> (anatase form) is in the middle of the pH scale (6.8 ± 0.2).<sup>14,25,42</sup> In general, it means that the adsorption of cations proceeds when the solution pH is higher than the pH<sub>PZC</sub> of TiO<sub>2</sub> and the adsorption of anions proceeds when the solution pH is lower than the pH<sub>PZC</sub> of TiO<sub>2</sub>.



Since both inorganic antimony species are oxyanions, the pH values of model solutions prior to adsorp-

tion were changed from 1.2 to 6.2. The results (see Fig. 2) show similar behaviour and recovery around 96.5 ± 3.0% for the both species at pH lower than 4.5. At higher pH values, recoveries were slightly decreased. For pH values lower than 3.0, a relative standard deviation (RSD) less than 5% was achieved. At higher pH, the RSD was measurably increased. Finally, a pH of 2.0 ± 0.1 was chosen and used in subsequent experiments.

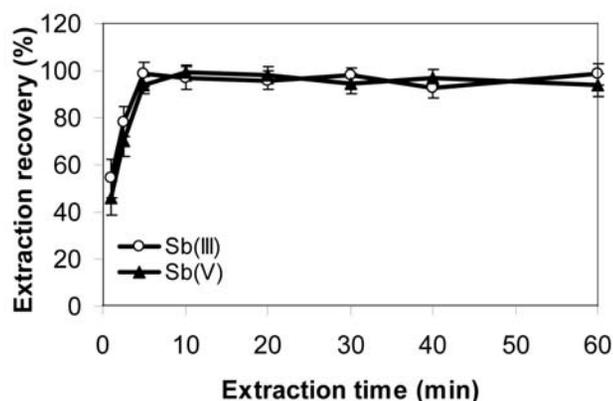


**Figure 2.** Effect of pH on the extraction recovery of Sb(III) and Sb(V). Applied conditions: initial sample volume: 50 mL; concentration of Sb(III) and Sb(V) in model solutions: 2.0 µg L<sup>-1</sup>; mass of nano-sized TiO<sub>2</sub>: 50 mg; extraction time: 30 min; preconcentration factor: 10.

Another factor which can be affected by the pH of the media is the stability of the TiO<sub>2</sub>-slurry.<sup>33</sup> At a pH lower than the PZC of TiO<sub>2</sub>, the action among the same positively charged ions (see eq 1) can keep the slurry stable. In our experiments, the final slurry solutions were prepared in DDW. At an initial pH of the model solutions of 2.0 ± 0.1, the final pH of the slurry solutions prepared in DDW was 2.5 ± 0.2 and the TiO<sub>2</sub>-slurry remained stable for at least 10 min (see results in Table 4). Therefore, the pH adjustment of the final TiO<sub>2</sub>-slurry was unnecessary. To ensure the stability of the TiO<sub>2</sub>-slurry after longer standing (in a HDPE bottle used for extraction), the slurry sample was agitated for 1 min again and then transferred into an autosampler cup (just before injection into a graphite tube).

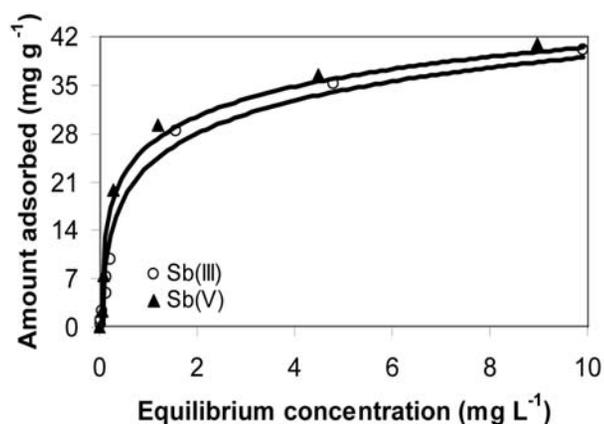
The effect of the extraction time on the extraction recovery of both inorganic antimony species was investigated in the range of 1–60 min. The results (see Fig. 3) show a similar behaviour for both species in all the studied range. Using an extraction time less than 5 min, low recoveries and high RSDs were obtained. An extraction time of 10 min was chosen and used in further experiments (obtained recoveries more than 95% and RSDs less than 5%).

To determine the adsorption capacity of nano-sized TiO<sub>2</sub>, model solutions (50 mL) having different Sb(V) and Sb(III) concentrations (in the range of 0.1–50 mg L<sup>-1</sup>) were adjusted to pH 2.0 ± 0.1 and the optimized SPE procedure described above applied. After centrifugation, the



**Figure 3.** Effect of extraction time on the extraction recovery of Sb(III) and Sb(V). Applied conditions: initial sample volume: 50 mL; concentration of Sb(III) and Sb(V) in model solutions:  $2.0 \mu\text{g L}^{-1}$ ; mass of nano-sized  $\text{TiO}_2$ : 50 mg; pH of the model solutions:  $2.0 \pm 0.1$ ; preconcentration factor: 10.

solutions were decanted and used for the determination of Sb by ICP-OES. The profile of the adsorption isotherms for Sb(V) and Sb(III) were obtained by plotting the equilibrium concentration of Sb ( $c_e$  in  $\text{mg L}^{-1}$ ) versus the amount of Sb adsorbed per unit weight of nano-sized  $\text{TiO}_2$  at equilibrium ( $q_e$  in  $\text{mg g}^{-1}$ ). The isotherms are shown in Fig. 4. Comparing the Langmuir and Freundlich isotherm models, it was found that the adsorption of Sb(V) and Sb(III) on nano-sized  $\text{TiO}_2$  correlated well ( $r > 0.998$ ) with the Langmuir equation. Finally, the maximum adsorption capacities of nano-sized  $\text{TiO}_2$  for Sb(V) and Sb(III) were determined from the linearized model of the Langmuir isotherm by using the plots of  $c_e/q_e$  against  $c_e$ . From the linear plot, the maximum adsorption capacity was calculated as the inverse of the slope. The maximum adsorption capacity of Sb(V) and Sb(III) on nano-sized  $\text{TiO}_2$  was found to be  $45.9$  and  $44.8 \text{ mg g}^{-1}$ , respectively.



**Figure 4.** Adsorption isotherms for Sb(III) and Sb(V). Applied conditions: initial sample volume: 50 mL; initial concentration of Sb(III) and Sb(V): in the range of  $0.1 - 50 \text{ mg L}^{-1}$ ; mass of nano-sized  $\text{TiO}_2$ : 50 mg; pH of the model solutions:  $2.0 \pm 0.1$ ; extraction time: 10 min; preconcentration factor: 10.

The achieved results showed similar behaviour of Sb(III) and Sb(V) under the conditions described above. Although all model solutions were prepared freshly and used for investigation immediately after preparation, there is the possibility that antimony can change its oxidation state during the extraction procedure. So, similarity in the achieved results can be a consequence of the change. This precondition surely needs a deeper investigation. Anyway, we can conclude that the selected experimental conditions are appropriate for separation and preconcentration of total inorganic antimony. To confirm the conclusion, model solutions prepared by mixing of Sb(III) and Sb(V) (1:1) were used in further experiments. However, since in general only Sb(V) is found in fresh waters<sup>43</sup>, synthetic fresh waters were spiked with Sb(V).

The effect of coexisting ions on the extraction recovery of total iSb was investigated in “simple” and “mixed” model solutions under the optimal extraction conditions (mass of  $\text{TiO}_2$ : 50 mg; pH:  $2.0 \pm 0.1$ ; extraction time: 10 min; PF: 20). The “simple” model solutions contained  $1.0 \mu\text{g L}^{-1}$  of iSb (Sb(III):Sb(V) in ratio 1:1) and a potentially interfering ion (each at three concentration levels:  $0.01 \text{ mg L}^{-1}$ ,  $0.10 \text{ mg L}^{-1}$ , and  $1.00 \text{ mg L}^{-1}$ ). Studied elements were: Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, and Zn (all as nitrate). In this case, no differences were observed in the extraction recovery achieved for iSb prepared in DDW and iSb in the presence of the potentially interfering ion studied (recoveries in the range of 90–110% were achieved). The “mixed” model solutions were prepared by dissolution of the chemicals listed in Table 2 in 1.0 L of DDW to produced five types of synthetic fresh water (SFW; very soft water (VSW); soft water (SW); moderately hard water (MHW); hard water (HW); and very hard water (VHW)). The samples of SFWs spiked with  $5.0 \mu\text{g L}^{-1}$  of Sb(V) were subjected to the optimized SPE procedure by using PF 10. The results obtained can be seen in Table 3.

**Table 3.** Determination of total iSb in synthetic fresh waters (SFWs) after SPE separation and preconcentration.

SFW	Total iSb determined $\pm$ SD ( $\mu\text{g L}^{-1}$ )	RSD (%)	Extraction recovery $\pm$ SD (%)
DDW	$4.96 \pm 0.16$	3.23	$99.1 \pm 3.2$
VSW	$4.83 \pm 0.19$	3.93	$96.7 \pm 3.8$
SW	$4.72 \pm 0.17$	3.60	$94.5 \pm 3.4$
MHW	$4.94 \pm 0.20$	4.05	$98.9 \pm 4.0$
HW	$4.69 \pm 0.11$	2.35	$93.7 \pm 2.2$
VHW	$4.53 \pm 0.13$	2.84	$90.6 \pm 2.6$

The figures of merit for the optimized SPE procedure are given below (with preconcentration factors of 10, 20, or 30, calculated as the ratio between the initial sample volume and volume of the slurry prepared according

to the described procedure). The RSD obtained for 10 samples of  $1.0 \mu\text{g L}^{-1}$  iSb (Sb(III):Sb(V) in ratio 1:1) subjected to the procedure with PF 30 was 4.2%. The detection limit, calculated according to 3 criteria, for 10 replicates of a blank solution by using PF 30, was  $0.10 \mu\text{g L}^{-1}$ . A certified reference material for trace elements in lake water TMDA-61 was used for checking the accuracy of the optimized method. For this purpose, the CRM was diluted 30 times and PF 30 was subsequently used. The mean determined value  $\pm$  SD was  $30.9 \pm 1.3 \mu\text{g L}^{-1}$  ( $n = 10$ ), while the certified value  $\pm$  SD was  $32.0 \pm 0.50 \mu\text{g L}^{-1}$ . An extraction recovery of 96.6% was achieved. Diluted TMDA-61 was also used for checking the stability of the prepared slurry. Results achieved after ten injections of the slurry solution with no agitation between injections can be seen in Table 4. The mean determined value  $\pm$  SD was  $30.2 \pm 1.1 \mu\text{g L}^{-1}$ . The obtained RSD was 3.6%.

**Table 4.** Checking the stability of the prepared slurry.

Injection	Determined Sb ( $\mu\text{g L}^{-1}$ )
1 <sup>st</sup>	31.3
2 <sup>nd</sup>	31.2
3 <sup>rd</sup>	30.5
4 <sup>th</sup>	29.0
5 <sup>th</sup>	28.9
6 <sup>th</sup>	31.4
7 <sup>th</sup>	30.3
8 <sup>th</sup>	29.3
9 <sup>th</sup>	29.0
10 <sup>th</sup>	31.1

**Table 5.** Determination of total iSb in natural mineral waters (NMWs) and natural creek water (NCW) after SPE separation and preconcentration.

Sample	PF* used	Determined Sb $\pm$ SD ( $\mu\text{g L}^{-1}$ )	RSD (%)
NMW1	20	$1.95 \pm 0.07$	3.6
NMW2	30	$0.98 \pm 0.07$	7.1
NMW3	30	$0.78 \pm 0.06$	7.7
NMW4	30	$1.21 \pm 0.06$	4.9
NCW	10	$8.38 \pm 0.19$	2.3

\*PF – preconcentration factor

The optimized SPE procedure was applied for the determination of total iSb in local water samples involving natural mineral waters (NMWs) from different parts of Slovakia and natural creek water (NCW) from a creek near a mine dump in Pezinok (abandoned mining area). The SPE procedure with PF 10, 20, or 30 was used and the results obtained are shown in Table 5. Finally, the NCW sample was used for the direct determination of antimony by ETAAS (no preconcentration and use of the temperature program shown in Table 1) and direct determination

of antimony by HGAAS (after reduction of Sb(V) to Sb(III) by using a mixture of 20% (m/v) KI and 10% (m/v) ascorbic acid). From the results shown in Table 6, an excellent agreement can be seen.

**Table 6.** Determination of antimony in natural creek water (NCW) by three methods.

Method used	Determined Sb $\pm$ SD ( $\mu\text{g L}^{-1}$ )	RSD (%)
direct ETAAS	$8.15 \pm 0.32$	3.9
direct HGAAS	$8.58 \pm 0.22$	2.6
the optimized $\text{TiO}_2$ -slurry ETAAS	$8.38 \pm 0.19$	2.3

## 4. Conclusion

In present work presented a relatively simple and rapid method for the determination of trace amounts of total inorganic antimony was optimized. For this purpose, a combination of batch experiments using nano-sized  $\text{TiO}_2$  (as a solid sorbent for the separation/preconcentration of total iSb) and direct slurry sampling ETAAS (for the determination of antimony after its adsorption onto nano-sized  $\text{TiO}_2$ ) was used. The extraction conditions for both inorganic antimony species (Sb(III) and Sb(V)) was carefully controlled. A PF of 10, 20, or 30 was used. At PF 30, a detection limit of  $0.10 \mu\text{g L}^{-1}$  and a RSD of 4.2% were achieved. The CRM for trace elements in lake water TMDA-61 was used for checking the accuracy of the optimized method. Finally, the optimized method was applied for the determination of total iSb in natural water samples involving mineral and creek waters.

The obtained results show that the presented procedure can effectively improve the analyte sensitivity and allow the determination of trace amounts of inorganic antimony. Using larger initial volumes of samples, higher preconcentration factors and lower detection limits can be obtained.

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## Povzetek

V članku je opisana ekstrakcija na trdni fazi z uporabo nano delcev TiO<sub>2</sub> kot trdnih nosilcev za predkoncentriranje/separiranje celokupnega anorganskega antimona (iSb) pred določitvijo z elektrotermično atomsko absorpcijsko spektrometrijo (ETAAS). Po adsorpciji antimona na nano delce TiO<sub>2</sub> se suspenzija direktno injicira v grafitno cevko. Določeni so bili pogoji za ekstrakcijo obeh antimonovih zvrsti (Sb(III) in Sb(V)) in interferenčni vplivi nekaterih ionov. Pravilnost postopka je bila preverjena s certificiranim referenčnim vzorcem (CRM- TMDA-61). Izdelana metoda je bila uporabljena za določevanje antimona v naravnih vodah in sintetskih vzorcih.