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Antimony(V) volatilization with bromide and determination by inductively coupled plasma atomic emission spectrometry

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Abstract

Antimony(V) is volatilized by reaction with potassium bromide in concentrated sulfuric acid media. After volatilization, the gases can be transported to an inductively coupled plasma spectrometer for atomic emission of antimony and its analytical determination. The influent factors, concentrated sulfuric acid volume, concentration and volume of the potassium bromide aqueous solution and carrier gas flow were investigated and optimized using different alternatives. A detection limit of 48 $\mathrm{ng\,ml^{-1}}$ of Sb was achieved under the optimized conditions with a precision of 7.6% and the calibration graph was linear from 0.10 to 10.0 $\mu\mathrm{g\,ml^{-1}}$ for a sample injection of 130 μl.

The study of interferences from common cations and anions revealed a good tolerance for most ions, although there was a significant improvement in Sb(V) volatility when As(III) was present. Furthermore, the As(III) sensitization was only produced with Sb(V) species, while the volatility of the Sb(III) bromide species was unaltered.

The method was applied to the determination of Sb in real river waters. The results were checked using alternative atomic spectroscopy methods.

Keywords: Sb(V) chemical bromide vaporization; River-water antimony(V) determination; ICP-AES

1. Introduction

Inorganic antimony determination is an analytical task of particular interest because of the risk to humans and its dependence on the oxidation state [1]. The analytical tendencies of antimony determination and speciation, summarized in recent reviews [2–4], show the use of two main methodologies, which can be classified as discontinuous or continuous methods.

In discontinuous methods, samples are pre-treated to separate individual fractions or to adapt samples to suitable determinations. Processes such as solvent extraction/concentration, precipitation, co-precipitation or adaptation with sonication have all been used. Determinations are subsequently carried out in the individual fractions mainly by atomic spectroscopy techniques [5,6] although other instrumental techniques, like neutron activation, have also been applied [7].

In the second approach, or continuous methods, antimony samples are submitted to procedures without physical separation of sample fractions. These methodologies have an advantage over discontinuous methods because the possible risks of loss and/or contamination are avoided. Methods reported include on-line techniques combination, mainly chromatography such as HPLC, GC, or solid phase extraction (SPE) [8], hyphenated with sensitive detections using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS) [9,10]. The main drawback is the need to use at least two highly sophisticated hyphenated instruments.

The antimony determination by chemical vapour generation (CVG) technique, in particular the most standard methodology based on the stibine hydride generation (HG),

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combined with atomic spectroscopy sources, such as flame-atomic absorption spectrometry (FAAS) [11], ICP-AES [12] or ICP-MS[13], has widely been applied because is very sensitive and permits separation and measurement reducing the complexity of the instrument hyphenation. However, the stibine is only obtained from Sb(III), whereas Sb(V) should be pre-reduced to Sb(III) [14,15]. Consequently, HG allows the speciation of both oxidation states but using a two steps determination: (i) total Sb and (ii) specie Sb(III) determination.

A new alternative chemical volatilization of both inorganic states of antimony, Sb(III) and (V), by halide generation has recently been appeared. It was reported that Sb(III) can be vaporized by bromide and determined by ICP-AES [16]. It was also mentioned that Sb(V) could be volatilized. In this paper, the Sb(V) vaporization by bromide is described. This behaviour represents a significant difference respect to the HG methods restricted to the Sb(III) volatilization.

The here reported halide Sb(V) volatilization is used to its determination by ICP-AES following a similar principle to that bromide Sb(III) vaporization [16], and other methods producing volatile halides for atomic spectrometric determinations [17], but the study shows specific characteristics for Sb(V).

The new proposed method was applied to an almost direct Sb determination in environmental river water samples, with Sb content in the order of ng ml^{-1}, decreasing the sample preparation steps.

2. Experimental

2.1. Apparatus

The instrumentation and the optimized conditions for the ICP-AES spectrometer operation and for generation of the volatile are given in Table 1.

The system used for the discontinuous generation of volatile antimony(V) was similar to other set-ups previously described [16]. It basically consists of PTFE reaction vessel, which has a gas inlet for the injection of reagents. The outlet of the vessel is directly connected to the injector tube of the plasma torch.

In the volatilization procedure, concentrated sulfuric acid was first put in the vessel. Then, the aqueous sample solution and the aqueous bromide solution were injected using a manual FIA injection valve acting the Ar nebulization gas as the carrier. The volatile generated was directly transported to the plasma torch. During volatilization, the spectrometer was fixed to the antimony emission wavelength (217.581 nm) and the emission intensity displayed and measured in an analogic recorder. Nylon and PTFE tubing were used in the mounting.

2.2. Software

The following software packages were used during this work: Statgraphic version 3.1 of Statgraphic, Systat version 2 of Systat Inc., MSM Simplex optimization written by us in Basic (Microsoft Quick Basic 1.0, Microsoft Corp.), WinNN version 0.97 by Y. Danon, for neural network simulation.

Table 1
ICP atomic emission spectrometer operating conditions and optimized conditions for bromide volatile generation

ICP-AES spectrometer	Perkin-Elmer P-40 (Shelton, CT, USA)
Torch	Demountable, type Perkin-Elmer
Injector tube	Alumina
Recorder system	Strip chart recorder Omniscribe D5117-2 (Belgium)
Spectrometer operating conditions	
RF (MHz)	40
Incident power (kW)	1
Antimony emission line (nm)	217.581
Ar (99.995%), flow rates:	
Outer (l min^{-1})	12
Intermediate (l min^{-1})	0.6
Observation height (mm) (above the load coil)	15
Volatile generation: Sb(V)–Br	
Volume Sb(V) sample solution (μl)	130
Volume concentrated sulfuric acid (μl)	615
Volume KBr solution (μl)	130
Concentration KBr solution (%, w v^{-1})	8.5
Carrier Ar gas flow rate (l min^{-1})	0.9

2.3. Reagents

A 1000 mg l^{-1} Sb(V) solution was prepared by dissolving 0.3342 g of antimony (V) oxide (99.995%) (Aldrich) and final dilution to 250 ml in volumetric flask with 2.5 M hydrochloric acid.

Potassium bromide solutions were prepared as required by dissolution of the solid salt in de-ionized water. Concentrated hydrochloric (37%, w/w), nitric (60%, w/w) and sulfuric (96%, w/w) acids (Merck) were of analytical reagent grade. De-ionized water of 18.2 MΩ cm of purity from a Milli-Q water system was used. All other chemicals used were also of analytical reagent grade.

2.4. Pre-treatment of river water samples

The water (25 ml) was only acidified in a beaker with 3 ml of concentrated sulphuric acid and heated and evaporated until the volume was reduced to 10 ml. Then, it was transferred to a 25 ml volumetric flask and diluted to the mark with de-ionized water. Aliquots of 130 μl of these solutions were taken for analysis.

3. Results and discussion

3.1. Variables affecting the method: optimization

The method developed consists of a discontinuous injection of aqueous Sb(V) and bromide (KBr) solutions onto a discrete volume of concentrated sulfuric acid, using a small PTFE reaction flask. After reaction, the gaseous products are transported by an Ar carrier gas flow to an ICP-AES spectrometer torch for the atomic emission of Sb. The experimental mounting is similar to other set-ups published in the bibliography [16].

Taking the parameters of the standard ICP-AES spectrometer and the experimental mounting into account, the potential variables influencing the emission signals of the method were:

S: volume of concentrated sulfuric acid (95–97% w/w);
B: volume of potassium bromide solution;
C: concentration of the KBr solution;
F: flow rate of the Ar carrier gas.

Other variables were previously studied and fixed as suitably as possible according to previous experience. The volume of the injected antimony sample solutions was fixed and maintained constant at 130 μl.

The significance of the four selected variables on the Sb emission intensity signals, and the exploration of the experimental domain, was studied using chemometric techniques of experimental design. A central composite design (CCD) was applied for this purpose. It comprises 2^4 experiments corresponding to a full factor design plus 8 experiments corresponding to a star and 3 experiments corresponding to centre points. The resulting 27 experiments were run in random order. This design was also used for assessing the influence on the signal apparition time.

The influence of the variables on the emission signal was determined and ranked, according to their standardized influences. It is gathered in the Pareto chart of Fig. 1.

It can be seen that the volume of bromide solution has the greatest effect, albeit negative, that is, the volatile is favoured at the lowest volume of bromide solution. The volume of sulfuric acid has a similar effect, but positive, which means that the highest signals are obtained at the highest volume of acid. It can also be observed that certain interactions concerning the flow of Ar and the concentration of KBr are almost statistically significant. It was therefore concluded that the best knowledge of the method should include the four variables.

After the experimental design, two optimization methods were applied to determine the optimum conditions of variables yielding the maximum signal: artificial neural network with back-propagation algorithm (ANN-BP) and simplex-MSM modification [18].

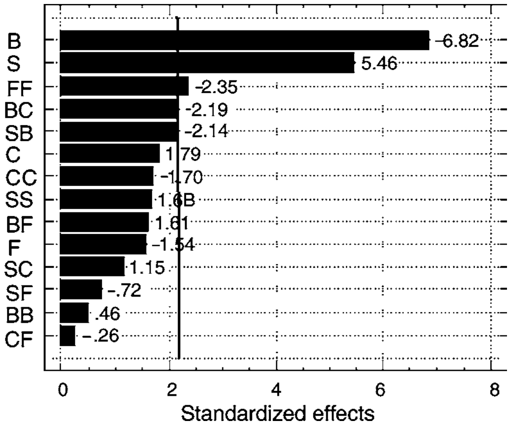

Fig. 1. Pareto chart for the standardized effects on the emission signals. The vertical line indicates the statistical significance bound for the effects: *S*, volume of concentrated sulfuric acid, *B*, volume of KBr solution, *C*, concentration of KBr solution, and *F*, flow of Ar carrier gas.

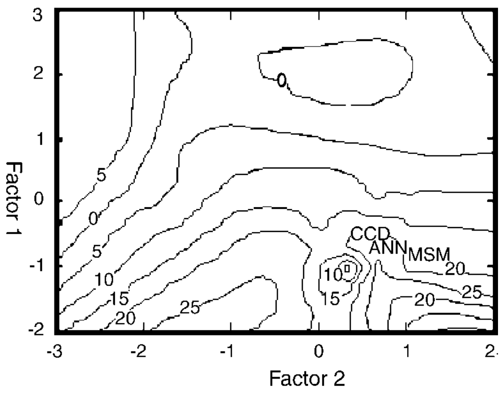

Fig. 2. Projection and location of the optimum corresponding to CCD, ANN-BP and MSM optimizations, over the iso-response map of the experimental domain derived by reducing variables using principal component analysis [20].

The theoretical ANN-BP optimization [19] was carried out using the results of the CCD as training and test sets. The average of its results is gathered in Table 2.

For MSM optimisation, the boundary conditions and restrictions for variables and signals were initially defined according to previous experiments. Only one MSM optimization was run from the most suitable initial point and the result is also gathered in Table 2.

The results of the different optimizations are projected over the response surface of the experimental domain and can be compared. It can be seen, in Fig. 2, that the optimum

Table 2
Optimum values of variables yielding maximum antimony signals obtained by the three different optimization methods: CCD, ANN-BP and MSM

Optimization method	Optimum values of the variables			
	S, volume of sulfuric acid (μl)	*B*, volume of KBr solution (μl)	*C*, concentration of KBr solution (% (w/w))	*F*, flow of Ar carrier gas (l min^{-1})
CCD	680	100	7.0	1.0
ANN-BP	615–630	95	7.2–8	0.7–0.9
MSM	615	130	8.5	0.9

Table 3
Effect of potential interferences on Sb(V) determination

Cation	Interfering ratio: [Cation]/[Sb(V)] (μg ml^{-1}/μg ml^{-1})	Anion	Interfering ratio: [Anion]/[Sb(V)] (μg ml^{-1}/μg ml^{-1})
Na(I)	40 (d)	Acetate	>40,000 (i)
NH_4(I)	>400	Bicarbonate	>400
Ca(II)	>400	Chloride (acid)	70,000 (i)
Cd(II)	>400	Fluoride	>10,000
Co(II)	>400	Iodide	1 (i)
Cu(II)	>400	Nitrate (acid)	8000 (d)
Mg(II)	>400	Perchlorate(acid)	>200,000
Sn(II)	40 (d)	Phosphate (acid)	>40,000 (i)
Al(III)	>400		
As(III)	1 (i)	Hydrogen peroxide	>10,000 (d)
Se(IV)	>400 (i)	L-Cysteine	>6000 (d)
Si(IV)	>400		

Sb(V) 0.50 μg ml^{-1} solutions were always added as reference. Interfering effects: increasing (i) or decreasing (d) signals.

are nearly located despite their different principles but MSM produced the highest signals. After all, for further investigations the conditions corresponding to MSM optimization were chosen as the most suitable.

On the other hand, the study about the influence of variables on the apparition time of the signals indicated that only the Ar flow effect was significant and negative. In other words, a low Ar flow favours signals.

3.2. Interferences

Sb(V) volatilization selectivity was evaluated by studying the effect of common anions and cations on the antimony signals. The influence of cations (chloride or sulfate preferable salts) on a test reference sample, always containing 0.5 μg ml^{-1} of Sb(V), was systematized in three series of solutions: the first series contained cations in a 1:1 concentration ratio in relation to Sb(V), the second series had cations in a 40:1 excess concentration ratio in relation to Sb(V) and the last series contained cations in a 400:1 high excess concentration ratio. The anions (sodium or potassium preferable salts) were always assayed in a high concentration ratio in relation to Sb(V). Variations above ±10% in the analytical signal of antimony in the presence of foreign ions were considered interferences. The results of the interference study, gathered in Table 3, show a high tolerance for ions with the following exceptions.

Na(I) produces a moderate decrease at high levels of concentration. The behavior is due to the salting-out effect.

The reductant behaviour of Tin(II) produces a moderate signal decrease which becomes constant at high concentration levels. This can be explained by its reduction to Sb(III) and, although it can also be volatilized by bromide [16], its signals are lower than Sb(V).

As(III) causes an increase in sensitivity which became a two-fold enhancement of signals for a 400:1 concentration ratio. This influence was studied in depth and the results are presented later.

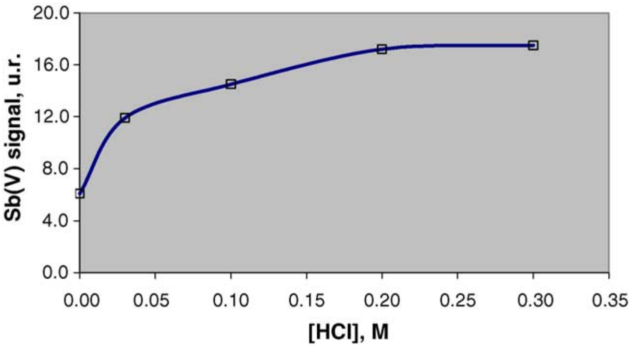

Fig. 3. Hydrochloric acid influence on the volatilization of 0.5 μg ml^{-1} Sb(V) in the presence of 200 μg ml^{-1} As(III).

Iodide produced a significant increase in signal and was practically constant in the range studied. It was considered to be due to complex volatile formation with halide mixture. This influence has also been detected in other volatile halides [16].

Nitrate produced a significant decrease in signals even at low concentration ratios, which was attributed to its oxidant effect, which prevents the reaction with bromide ions because it is easily oxidized to bromine in sulfuric acid media.

Hydrogen peroxide behaves in a similar way to nitrate, but less intensely, which was always attributed to its oxidant properties.

Phosphate significantly enhanced signals, which was considered as consequence of its acid media and the releases of an important aqueous dilution heat, similar but less strongly than sulfuric acid. Consequently, it favours the volatilization.

L-Cysteine was studied because of its selective reductant behavior for Sb(V) to Sb(III). Its presence decreases Sb(V) signals at concentration ratios of about 2000:1, but does not eliminate them. This behaviour seems to confirm a reductant effect similar to that of Sn(II).

In conclusion, the interference study showed that oxidant compounds (acting on bromide) decrease sensitivity and may even totally eliminate the antimony signals. Reductant compounds (acting on Sb(V)) also decrease signals but do not eliminate them. In other hands, increased sensitization may be found with iodide, arsenic (III) and also phosphoric acid.

3.3. The As(III) effect

Improved Sb(V) volatilization with bromide in the presence of As(III) was very significant and confirmed in a separate study. It was observed that it depends on the acidity of the media and the ratio [As(III)]/[Sb(V)].

The acidity of the reaction media, defined as the hydrochloric acid concentration, was evaluated from experiments with a reference concentration of 0.5 μg ml^{-1} of Sb(V) and 200 μg ml^{-1} As(III) varying their HCl concentration in the range 0.03–0.3 M and always working at optimum values of the other variables. The results, gathered in Fig. 3, show that hydrochloric acid produces an increase of up to 200% in

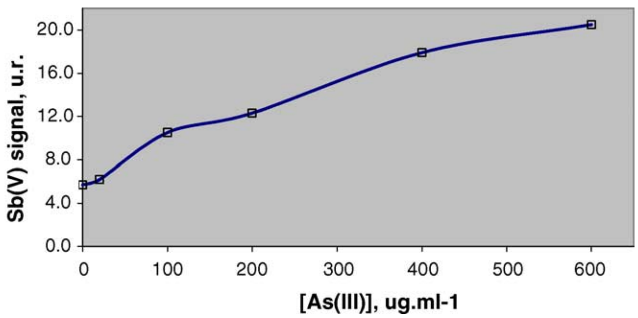

Fig. 4. Arsenic (III) influence on the Sb(V) signals using a reference solution with 0.5 μg ml^{-1} Sb(V) and 0.03 M HCl.

reference signals at 0.03 M HCl, and up to 300% at 0.2 M, with higher concentrations the effect remains practically constant.

In spite of the results, the 0.03 M concentration was selected as the most suitable for later experiments because it reduced mounting damage (mainly tubes and fittings) and favoured stability.

The [As(III)]/[Sb(V)] concentration ratio was also studied. It was varied between 40 and 1200 which corresponds to an [As(III)] range between 20 and 600 μg ml^{-1}. The experiments were carried out adopting the acidity of 0.03 M HCl with 0.5 μg ml^{-1} Sb(V) as reference. The results in Fig. 4 show that Sb(V) presents a significant signal increase, respect to reference signals, with a highest increase, by to 300%, when 600 μg ml^{-1} As(III) was added.

However, as with the HCl concentration, 200 μg ml^{-1} of As(III) was considered the most suitable concentration for later work after taking into account practical considerations of contamination and mounting stability.

Taking the aforementioned optimized values (0.03 M HCl and 200 μg ml^{-1} As(III)) a calibration experiment was studied with a Sb(V) range from 0.01 to 10.0 μg ml^{-1}. The values of antimony signals from solutions with and without As(III) addition, and also their ratio, are gathered in Fig. 5. It can be seen that, for the range 0.2–2.0 μg ml^{-1} Sb(V), the ratio between signals is practically 2.0. Experiments with lower Sb(V) concentrations, 0.01–0.05 μg ml^{-1}, showed as much as a 5.0-fold signal increase. However, experiments with higher Sb(V), 10.0 μg ml^{-1}, showed that the As(III) did not increase the antimony signal significantly. It is clear that the sensitization increased with increasing of [As]/[Sb(V)] ratio and a 2.0-fold enhancement is maintained constant in sensitized signals for the range 0.2–2.0 μg ml^{-1} Sb(V).

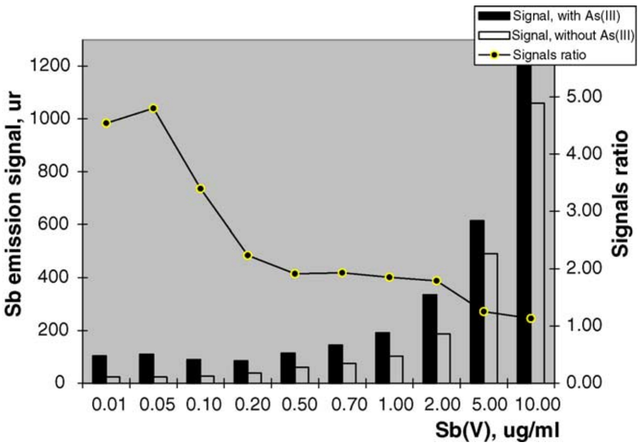

Fig. 5. Antimony (V) emission signals, with or without As(III), in relative units (ur) and ratio between signals.

An exact explanation to this effect is not possible in this moment. However, these results can indicate a possible modification in the kinetics of Sb(V)-halide reaction by As(III). This enhanced kinetic behaviour is not strange for Sb(V) because it is produced in other reactions related to his stibine generation [12].

In the other hand, the volatilization of Sb(III) with bromide in the presence of As(III), using its best optimum conditions [16] or the Sb(V) conditions here reported, was also studied. It was found that Sb(III) is volatilized in both conditions but its volatilization was not modified by As(III) and, consequently, the sensitization is only effective, selective, towards Sb(V).

A detailed study, of the Sb(V)–(III) differential bromide volatilization, is in progress in order to obtain their direct speciation.

3.4. Volatilization efficiency

The volatilization yield of Sb(V) was determined by generation of the volatile from a 10.0 μg ml^{-1} Sb(V) solution with only bromide and sulfuric acid at optimum conditions The gases evolved were trapped in a 0.1 M NaOH alkaline solution and both the initial reaction solution and the trapping solutions were analyzed for their Sb content, by standard ICP-AES with pneumatic nebulization (PN) of solutions.

The best results of the volatilization experiments gave an average loss of 50% of Sb(V) in the reaction vessel. However, the Sb recovered in the trapping solution was in the order of 10%. The results allow to calculate a transport efficiency in the order of 20% and a total yield for the Sb introduction in the ICP in terms of 10% (possible loss by inefficient absorption can also be included). The values can be considered of interest because but they represent a significant yield enhancement in sample introduction respect to standard methods of PN.

In the other hand, the values are an agreement with yields published in Sb(III) bromide volatilization [16].

3.5. Sensitivity, reproducibility and linear working range

The analytical performance for this new method based on injections of 130 μl Sb(V) and bromide solutions in sulfuric acid media at optimum conditions for volatilizing Sb(V) and measuring the discontinuous Sb emission intensity at 217.581 nm by ICP-AES was evaluated by preparing a calibration curve and running the ICP-AES spectrometer at the conditions given in Table 1.

The emission intensity was found to be linear up to 10.00 μg ml^{-1} Sb(V). With an equation of

$Y = 4.39 + 103.52X$, the regression coefficient was 0.9974. Y is the height of the antimony emission peak in arbitrary units and X is the concentration of Sb(V) in solution in μg ml^{-1}.

The signals display typical 'transient' shape with apparition times of around 2 min after the last reagent injection.

The relative standard deviation obtained by analyzing six independent replicates of 0.5 μg ml^{-1} Sb(V) was 7.6%.

The instrumental detection limit (LD) (3 s) was 48 ng ml^{-1} Sb(V) and it is comparable with that obtained by standard procedures using continuous PN sample introduction coupled with ICP-AES(LD in the order of 20–40 ng ml^{-1}) but is one order of magnitude higher than those achieved by continuous HG-ICP-AES (LD about 5 ng ml^{-1} [12]). However, it should be pointed out that the conditions in this procedure refer to a batch method which for a discrete injection of 130 μl sample solution represents a significant low absolute detection limit of 6.2 ng Sb(V).

3.6. Application

Total Sb was first determined in a natural river water by graphite furnace- atomic absorption spectroscopy(GF-AAS) (in conventional conditions). The Sb level found was lower than the limit of detection of the method, that is, <16 ng ml^{-1}.

Determination of Sb was also made by the new proposed method using the conditions described in Table 1. The analysis was directly performed on samples without pre-treatment but Sb could not be detected, probably due to the nitrate content, which inhibits the Sb signal.

Consequently, a conditioning step was performed by gently heating and treating the sample solutions with sulfuric acid in order to remove the nitrate. The solutions were then re-diluted to the initial volume with de-mineralized water. It is important to note that, as consequence of this step, Sb(III) should be oxidized to Sb(V).

After pre-treatment, different sub-samples were analyzed by normal bromide volatilization and also by the sensitization with As(III) using its optimum conditions. The concentration of Sb(V) in samples was lower than 16 ng ml^{-1} which confirms an agreement between the GF-AAS and the new method. Recovery tests were also made by adding Sb(V) solutions. This study shows that the recoveries are quantitative by either the normal volatilization (93%) or the sensitized volatilization (100%), but the sensitization offers a better result than the former. Results are presented in Table 4.

Table 4
Determination of Sb in river water

River-water sub-sample	Spiked Sb(V) (ng ml^{-1})	As(III) effect	Found* Sb(V) (ng ml^{-1})	Yield Sb recovered (%)
1	–	yes	11.8	–
2	500.0	yes	512.0	100.0
3	500.0	–	475.0	92.8

* Results are the average of two replicates.

4. Conclusions

This method demonstrated that the chemical volatilization of antimony(V) with bromide can be used as a reliable gas sample introduction method in ICP-AES. The Sb(V) determination, by this method, presents the following advantages:

- With a discrete sample injection, its LD is in the order of ICP-AES methods with continuous pneumatic nebulization.
- The method is less susceptible to interferences than HG.
- Volatilization can be sensitized by As(III) and HCl acid and this sensitization is effective for Sb(V), whereas Sb(III) is hardly modified.
- The method can be adapted to Sb(V) determination in natural river waters without significant sample pre-treatment.

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