



Mechanism of action of additives in chemical vapor generation of hydrogen selenide: Iodide and thiocyanate

Emanuela Pitzalis^a, Massimo Onor^a, Roberto Spiniello^a, Carlos Eduardo Mendes Braz^b, Alessandro D'Ulivo^{a,*}

^a C.N.R., Institute of Chemistry of Organometallic Compounds, S.S. of Pisa, Via G. Moruzzi, 56124 Pisa, Italy

^b Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos-SP, Brazil

ARTICLE INFO

Article history:

Received 11 December 2017

Received in revised form 10 April 2018

Accepted 12 April 2018

Available online xxx

Keywords:

Chemical vapor generation

Hydrogen selenide

Atomic absorption

Tetrahydridoborate

Mechanism

ABSTRACT

The chemical vapor generation of H₂Se has been investigated in the presence and in the absence of either NaI or NaSCN as additives (0.5 mol L⁻¹), in HClO₄ media (0.1–5.0 mol L⁻¹) and using a low concentration of NaBH₄ (0.02 mol L⁻¹). The enhancement of generation efficiency of H₂Se produced by iodide and thiocyanate was measured by a continuous flow reaction system coupled with a miniature argon-hydrogen diffusion flame and atomic absorption detection. The chemifold of the continuous flow reactor was designed in order to change the mixing sequence and the interaction time of the reagents. By this way it has been possible to evaluate the contribution of additive-selenium and additive-borane species to the mechanism producing the increase of generation efficiency of H₂Se. Both the iodide complexes of selenium and borane contribute to enhance generation efficiency of H₂Se, whereas the thiocyanate complexes of selenium rather than thiocyanate-borane complexes play a major role in the enhancement of the efficiency. At elevated acidities (2 < [H⁺] < 5 mol L⁻¹), only thiocyanate continues to maintain its properties to increase H₂Se generation efficiency while iodide causes a marked signal depression unless its addition is performed after the starting of Se^{IV}-[BH₄⁻] reaction with an appropriate time delay. Both iodide and thiocyanate caused marked depression of H₂Se generation when NaBH₄ was replaced by the amine boranes, NH₃-BH₃ and *tert*-ButylNH₂-BH₃.

© 2017.

1. Introduction

Chemical generation of volatile species (CVG) is one of the most important and powerful sample introduction technique for the determination and speciation of trace element by atomic or mass spectrometry [1–3]. Derivatization by aqueous tetrahydridoborate (–1), sodium or potassium salts (THB) is one of the most popular techniques for the generation of Hg⁰ and the volatile hydrides of As, Sb, Bi, Ge, Sn, Pb, Se and Te and, more recently the aim of CVG has been expanded to many transition and noble metals, even if with fewer analytical applications [3,4]. Amine boranes reagents, which are much more stable to hydrolysis with respect to THB, have been recently employed both for diagnostic and analytical applications [5–10].

In the recent years many works have been developed on fundamental aspects of CVG, with the aim of filling gaps on the knowledge of the mechanisms governing the CVG.

In order to understand the mechanism of CVG by borane complexes in aqueous media some key processes should be known in details. At first, it is important to understand the mechanism taking place under ideal conditions, which essentially are the mechanisms governing the two competitive reactions leading to formation of volatile derivatives:

- (i). the mechanism of hydrolysis of BH₄⁻ and borane complexes in aqueous media;
 - (ii). the mechanism of generation of volatile species by aqueous borane aqueous media.
- Then it will be necessary to understand how the processes (i) and (ii) can be modified in the presence of foreign species, that is:
- (iii). the mechanism of liquid phase interferences arising from foreign chemical species;
 - (iv). the mechanisms of action of additives, which are chemical species that are employed to modify the reactivity of a CVG system.

At present, mechanisms (i) and (ii) are known with a good degree of accuracy [4,11,12], and also (iii), the reactivity of aqueous boranes controlling interferences, have reached a good degree of rationalization [13]. The knowledge of mechanism (iii) and (iv) is of paramount importance for practical application of CVG. Considering that, in general, interferences and additives produce a perturbation of those processes which takes place in pure aqueous solution, mechanisms (i) and (ii), the studies of the mechanisms (iii) and (iv) have to face with an increasing degree of complexity due to all the possible mutual interactions among the species which are present in the reaction solution. In CVG, chemical additives are employed in order to modify the characteristic of the chemical reaction system and/or to achieve a better control of interferences [1], and their mechanism of action is even less known than the mechanism of liquid phase interference. In the

* Corresponding author.

Email address: dulivo@pi.iccom.cnr.it (A. D'Ulivo)

light of the knowledge of the mechanisms of CVG taking place in an unperturbed reaction system [4,11,12], an additive can act by modifying the structure of the analytical substrate, through complex formation or redox reactions and/or by modifying the structure of the borane reagent. These two possible interactions have been confirmed by the few dedicated experiments on the role of additive in CVG that have been reported in literature. In the case of L-cysteine (Cys), it is known that it can reduce the analytical substrate or forms complexes (thiolates), as well as it can form thiolate complexes with borane, RS-BH_3^- [14]. The interaction between Cys and BH_4^- could explain the signal enhancement in germane generation [15], the signal enhancement and the shift of optimal range of acidity for arsane generation [15,16]. On the contrary, shift of optimal range of acidity for stannane generation can be addressed to the interaction of tin with Cys, while the interaction of Cys with borane did not play any role [17]. The role played by oxidizing additives, persulfate, hydrogen peroxide, Ce^{IV} , permanganate, dichromate [18,19] and hexacyanoferrate (III) [20–23] in the enhancement of plumbane generation by reaction of THB with inorganic Pb^{II} , is still controversial. In this case it is not clear whether the observed effect can be addressed to additive-analyte interactions – redox reactions, $\text{Pb}^{\text{II}} \rightarrow \text{Pb}^{\text{IV}}$ [18,19] and $\text{Pb}^0 \rightarrow \text{Pb}^{\text{II}}$ [20–23] – or to additive-borane interactions [19,20] leading to formation of borane complexes which have a specific reactivity towards Pb^{II} substrates. The formation of additive-borane complexes has been also proposed in the case of bismuthane generation, where $\text{K}_3[\text{Fe}(\text{CN})_6]$ and Fe^{III} produce some signal enhancement, prevent the formation of non-volatile, insoluble side reaction products, assumed to be Bi^0 , and improve the linear range of calibration curves [24]. On the contrary, the same positive effects produced by thiocyanate on bismuthane generation were addressed to the formation of thiocyanate- Bi^{III} complexes [24].

In the CVG of hydrogen selenide by reaction of BH_4^- with inorganic Se^{IV} , Agterdenbos et al. [25,26] observed that the presence of 1 M halide ions, iodide, bromide and chloride in the reaction system allowed to decrease dramatically the concentration of BH_4^- that is necessary to obtain the maximum yield of hydrogen selenide, and improved the tolerance to interferences. The strongest effect was observed for iodide, followed in the order by bromide and chloride. In later experiments they showed that the addition of 0.1 M iodide to the THB solution had the effect that only 0.001% of THB solution was sufficient for complete conversion of Se^{IV} to H_2Se [27]. Agterdenbos and Bax [26] did not find any evidence that iodide perturbs the decomposition rate of THB and its effect was termed “catalytic” because it clearly speeds up the reduction kinetic of Se^{IV} to H_2Se . More recently, in addition to halides, the same “catalytic” role was confirmed also for thiocyanate, the effectiveness of which was intermediate between iodide and bromide [28]. The mechanisms that could play a role in controlling a such “catalytic” effect have been recently discussed [4] but no dedicated experiments have been reported to investigate the role played by additive- Se^{IV} and additive- BH_4^- interactions in determining the observed “catalytic” effect.

In the course of the last years several evidences on CVG of hydrogen selenide and the kinetics of hydrolysis of boranes in the presence of chemical additives have been collected in our laboratories. A selection of these evidences are reported and discussed in this paper with the aim to contribute to clarification of the role played by additives in CVG of hydrogen selenide.

2. Experimental and calculations

2.1. Reagents

Borane ammonia (AB), borane *tert*-Butylamine (TBAB) (assay 97%,) and NaBH_4 (THB) (assay 98%,) were from Sigma-Aldrich. NaOH (Pellets, 98%,) was from Fluka Chemika, Sigma-Aldrich. Stock solution of 1000 mg L^{-1} of selenite (H_2SeO_3 in HNO_3 , AS standard solution) was from Fluka. Analytical grade inorganic acids, 37% HCl, 65% HNO_3 , 65% HClO_4 and 96% H_2SO_4 , NaI, NaSCN and NaClO_4 , were from Carlo Erba. Stock solutions of 10% NaBH_4 were prepared in 1 mol L^{-1} NaOH and stored at 4°C . Working solution of the reductants (0.01–0.25 M) were prepared daily by appropriate dilution of the stock solution and stabilized by adjusting the final concentration of NaOH in the range of 0.005 to 0.1 M, depending on the experiment.

2.2. Apparatus and measurements

Experiments on the CVG of hydrogen selenide were performed using a continuous flow reaction system coupled with miniature hydrogen diffusion flame atomizer and atomic absorption spectrometric detection. Details of the apparatus are reported elsewhere [7]. The chemifold setups employed in the continuous flow reactor allow to achieve different mixing sequences of the sample and reagents are reported in Fig. 1. Mixing junctions are in Kel-F (Ismatec, 0.8 mm channel diameter) and all the tubings are in Teflon or Teflon PFA (0.8–1 mm i.d.). Reagent flow rates are 2 mL min^{-1} for THB and 4 mL min^{-1} for sample and additive solutions.

The absorbance, S_0 , obtained by reduction of 0.2 mg L^{-1} Se^{IV} in 1 M HCl with 0.25 M THB, employing the chemifold setup A (Fig. 1) was taken as reference signal, and the relative absorbance, S/S_0 , was taken as a measure of the relative generation efficiency of hydrogen selenide.

The rate of hydrogen gas generated by the hydrolysis of borane complexes was measured by monitoring the pressure, P , in the headspace of the reaction cell used for hydrolysis. Measurements were performed by using a 17.5 mL borosilicate glass, thermostated cell (25°C) described previously [29]. The cell was in borosilicate glass and was equipped with an injection port and pressure sensor (DS Europe, model LP625–1, 3.5 bar full scale). The measurements were performed by placing 2.0 mL of acid solution in the cell. A 1 mL plastic syringe was loaded with 0.6 mL of water followed by 0.4 mL of 0.2 M THB solution in 0.1 mol L^{-1} NaOH. This particular loading sequence allows complete and reproducible injections, avoiding that an uncontrolled amount of solution containing the borane remained in the injection port. Then the syringe was placed into the injection port, which comprised a manual on-off valve (Hamilton, small body) to avoid pressure losses. The solution was left under magnetic stirring and, after pressure signal stabilization, the THB was injected under constant stirring. The pressure signal was acquired for 1800 s at 10 s^{-1} . The pressure was corrected for a blank which is due to pressure increase caused by the contraction of headspace volume following the 1 mL injection. The blank was measured by placing 2 mL of H_2O in the reaction cell and injecting 1 mL of H_2O .

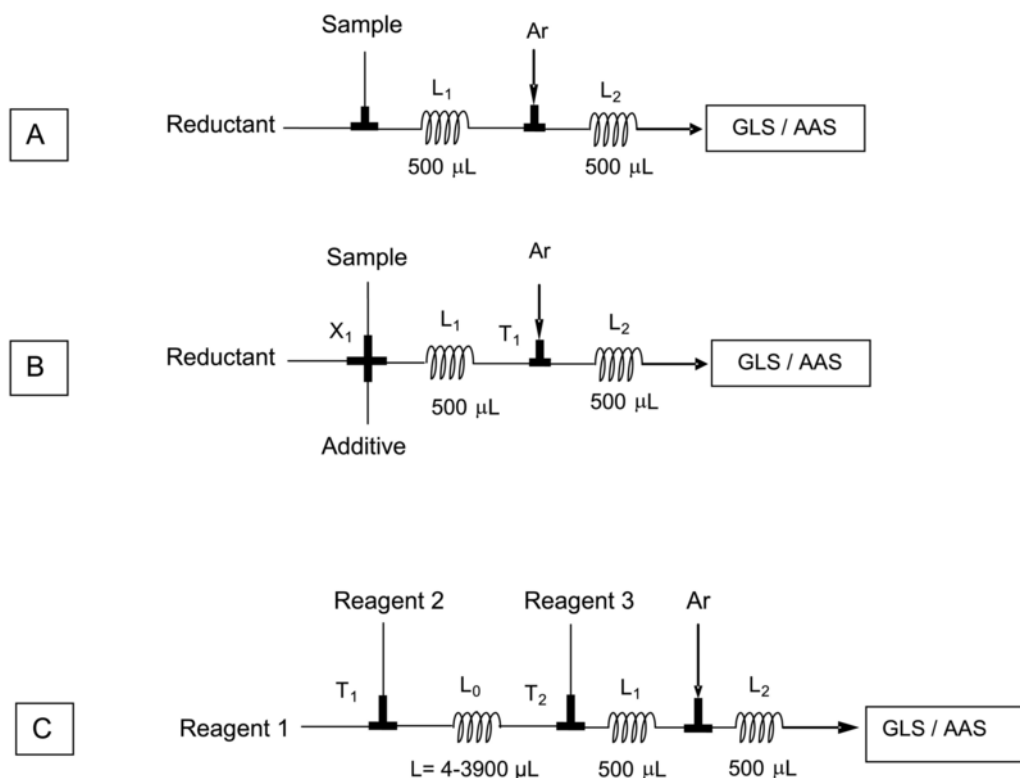
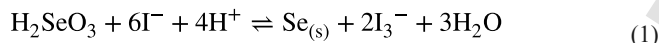


Fig. 1. Chemifold configurations employed in CVG-AAS for the investigation of the effect of different mixing sequences and reaction times of the reagents on the generation efficiency of H_2Se .

2.3. Calculations of the reaction rate of Se^{IV} reduction by iodide

The calculations relevant the reduction of Se^{IV} to Se^0 by iodide.



$$\alpha_{\text{Se}} = \frac{\text{Se}^{\text{IV}}}{(\text{Se}^{\text{IV}})_{t=0}} = e^{-k't} \quad (4)$$

$$\text{with } k' = [\text{H}^+]^2 [\text{I}^-]^3 / k_2.$$

were performed by using the kinetic law derived by Neptune and King [30]:

$$\frac{-d[\text{Se}^{\text{IV}}]}{dt} = \frac{[\text{H}_2\text{SeO}_3][\text{H}^+]^3[\text{I}^-]^4}{k_1[\text{I}_3^-] + k_2[\text{H}^+][\text{I}^-]} \quad (2)$$

With $k_1 = 5.7 \times 10^{-6} \text{ mol}^6 \text{ L}^{-6} \text{ min}$, and $k_2 = 1.85 \times 10^{-6} \text{ mol}^5 \text{ L}^{-5} \text{ min}$ ($T=0^\circ\text{C}$, 0.15 M ionic strength). It must be considered that the concentration of acid sample ($2.5 \times 10^{-6} \text{ mol L}^{-1}$ selenium in $0.1\text{--}5 \text{ mol L}^{-1}$, 4 mL min^{-1}) and iodide (0.5 mol L^{-1} , 4 mL min^{-1}) are halved after mixing in loop L_1 giving $\text{Se}_{\text{tot}} = 1.25 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{I}_3^-] \leq 2\text{Se}_{\text{tot}}$, $[\text{H}^+] \geq 0.05$ and $[\text{I}^-] = 0.1 \text{ mol L}^{-1}$. $gk_2[\text{H}^+][\text{I}^-] \gg k_1[\text{I}_3^-]$ and the Eq. (2) is reduced to the form:

$$\frac{-d[\text{Se}^{\text{IV}}]}{dt} = \frac{[\text{H}_2\text{SeO}_3][\text{H}^+]^2[\text{I}^-]^3}{k_2} \quad (3)$$

The fraction of Se^{IV} remaining unreacted at a given time, α_{Se} , can be calculated by applying the pseudo-first order approximation to Eq. (3):

3. Results and discussion

3.1. Effect of iodide and thiocyanate in CVG of H_2Se

In the absence of additives the generation of H_2Se from hydrochloric acid media is more efficient if compared to sulfuric, perchloric and nitric acid media. Using 0.25 mol L^{-1} THB and 1 mol L^{-1} acid concentration the relative generation efficiency of H_2Se , S/S_0 , is 0.9, 0.85 and 0.7 for H_2SO_4 , HClO_4 and HNO_3 , respectively. At 0.02 mol L^{-1} THB, S/S_0 is 0.5, 0.22, 0.20 and 0.06 for HCl , H_2SO_4 , HClO_4 and HNO_3 , respectively. Considering that in many experiments the effect of additives was investigated at variable acidity or reaction media, it seemed important the choice of an inorganic acid, as perchloric acid, whose anion presents non-complexing capacity. By this way the variation of S/S_0 vs acidity ($0.1\text{--}5.0 \text{ mol L}^{-1}$ HClO_4) cannot be addressed to the formation of analyte-perchlorate or borane-perchlorate complexes. Most of CVG-AAS experiments were performed by using 0.02 mol L^{-1} THB and variable HClO_4 concentration in the range from 0.1 to 5 mol L^{-1} .

Fig. 2 shows the effect of iodide and thiocyanate on the generation efficiency of H_2Se as a function of acidity, when all the reagents are mixed simultaneously. The signal enhancement is strongly dependent on acidity. Even if iodide works very well in the typically range of acidities used for selenium, i.e. $0.5\text{--}1.0 \text{ mol L}^{-1}$, at elevated acidities

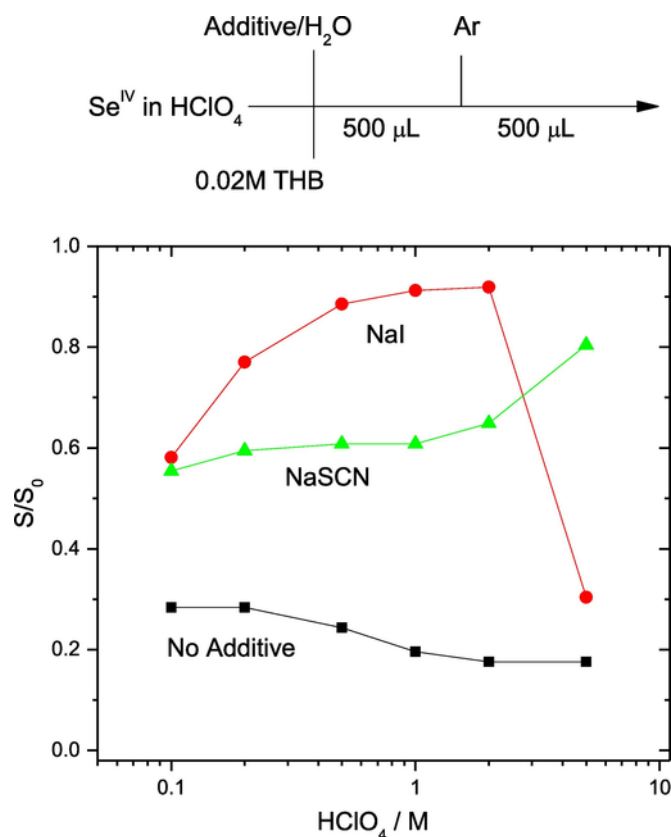


Fig. 2. Effect of sample acidity on the generation of H_2Se ($0.2 \mu\text{g mL}^{-1} \text{Se}^{\text{IV}}$), with and without additives, measured by CVG-AAS. All reagents mixed at the same time using chemifold setup B (Fig. 1). Additives = 0.5 mol L^{-1} , THB = 0.02 mol L^{-1} in $5 \times 10^{-3} \text{ mol L}^{-1} \text{NaOH}$.

is much less effective than thiocyanate. The effects reported in Fig. 2 are the result of one or more of the simultaneous reactions among all the species that are present in the reaction solution:

Table 1
Pressure of hydrogen measured after 30 min hydrolysis of THB.

Media	P (bar) ^a	P/P _∞ (%) ^b
0.1 M HClO ₄	0.53	98
0.1 M HClO ₄ + 1.9 M NaClO ₄	0.47	87
0.1 M HClO ₄ + 0.9 M NaClO ₄ + 1 M NaI	0.52	96
0.1 M HClO ₄ + 0.9 M NaClO ₄ + 1 M NaSCN	0.50	93
1 M HClO ₄	0.49	91
1 M HClO ₄ + 1 M NaClO ₄	0.46	85
1 M HClO ₄ + 1 M NaI	0.52	96
1 M HClO ₄ + 1 M NaSCN	0.46	85

^a 0.4 mL of 0.2 mol L^{-1} of THB ($80 \mu\text{mol}$) injected. See Section 2.1 for details. Pressure uncertainty better than 0.01 bar.

^b $P_{\infty} = 0.54 \text{ bar}$ is the expected hydrogen pressure generated by complete THB hydrolysis.

- THB with the solvent, leading to formation of reactive hydri-doboron species;
- hydri-doboron species with Se^{IV} , contributing to formation of H_2Se ;
- THB with the additive, leading to formation of modified borane/hydri-doboron species;
- Se^{IV} with the additive, leading to analytical substrate modification;
- between modified borane and/or hydri-doboron species with Se^{IV} and/or modified analytical substrate.

In the next sections several evidences will be reported and discussed to understand the possible contribution of reactions c - e in the enhancement of H_2Se generation in the presence of iodide and thiocyanate.

3.2. Effect of additives on the hydrolysis rate of THB

Agterdenbos and Bax [26] reported that the presence of 1 mol L^{-1} iodide did not change the decomposition rate of THB in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ or $2 \text{ mol L}^{-1} \text{HCl}$. This conclusion cannot be confirmed by the results of the experiments reported in Table 1 and, in particular, from those reported in Fig. 3, in which the rate of hydrolysis of THB was measured through the rate of hydrogen evolution in both 0.1 mol L^{-1}

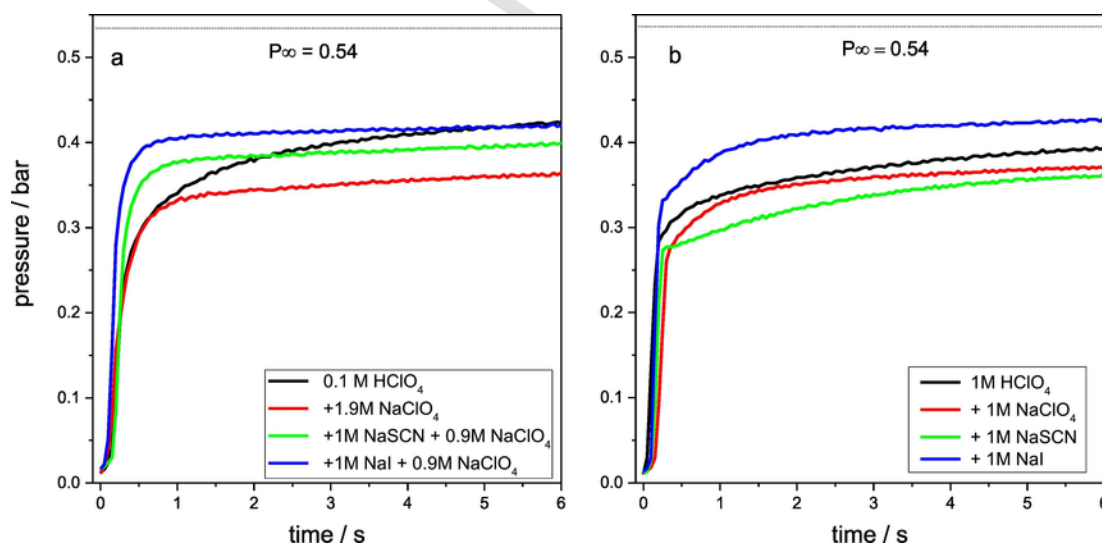
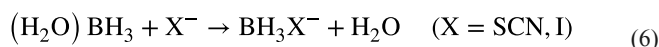
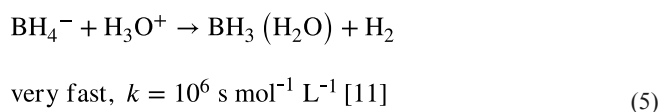


Fig. 3. Rate of pressure increase due to H_2 evolved following the addition of $80 \mu\text{mol}$ THB to 2 mL of hydrolysing acid solution. (a) $0.1 \text{ mol L}^{-1} \text{HClO}_4$ hydrolysing solution with and without different additives; (b) $1.0 \text{ mol L}^{-1} \text{HClO}_4$ hydrolysing solution with and without different additives. See Section 2.1. for experimental details.

and $1 \text{ mol L}^{-1} \text{ HClO}_4$. The use of perchlorate media excluded the possibility of borane complex formation involving the anion of the acid. Nevertheless, we found that the ionic strength affected the hydrolysis rate of THB and for this reason the kinetic experiments were performed by keeping constant the ionic strength at 2 mol L^{-1} with NaClO_4 . The rate of hydrogen evolution in the first seconds of hydrolysis is reported in Fig. 3 and it is of particular importance because it describes phenomena occurring in the same time scale of the continuous flow reaction system. The results of Fig. 3 support the hypothesis that the changes of the rate of hydrolysis of THB produced both iodide and thiocyanate can be reasonably addressed to the interaction of the iodide and thiocyanate ions with the hydrolysis mechanism of THB. The iodide speeds up the hydrolysis rate of THB at low and high acidities, whereas thiocyanate speeds up the rate of hydrolysis at the lower acidity of 0.1 M and slows down the rate at 1 mol L^{-1} acidity. This could be explained by the formation of analyte-borane complex during the first step of hydrolysis:



Concerning borane complexes of halide ions, their formation is reported for LiBH_3Cl [31], in the synthesis KBH_3F [32], and the ^1H NMR spectrum of LiBH_3I has been reported following the reaction of alkyl iodides with LiBH_4 [33]. Synthesis and characterization of MBH_3SCN with $\text{M}=\text{Li}, \text{Na}, \text{Ba}$ [30] and $\text{M}=\text{Na}, \text{NH}_4^+$ [34] have been reported. The different effect of acidity on the rate of hydrolysis of THB in the presence of iodide and thiocyanate (Fig. 3) could be explained by assuming that BH_3SCN^- and/or the related hydridoboron species which are formed from its hydrolysis, are more resistant to the hydrolysis than the similar compounds of BH_3I^- at elevated acidities.

It is therefore reasonable to conclude that the species BH_3I^- and BH_3SCN^- are formed during the hydrolysis of THB in the presence of the two additives and that they can play a role in the enhancement of generation efficiency of hydrogen selenide.

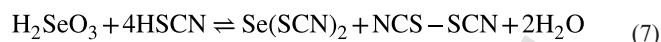
3.3. Effect of additive- Se^{IV} complexes on CVG of H_2Se

The reaction of both iodide and thiocyanate with inorganic Se^{IV} (selenous acid, H_2SeO_3) has been investigated and reported in the literature.

Neptune and King [30] investigated both the kinetic and mechanism of reaction of selenous acid with iodide ions (see reaction 1 and Eq. (2) in Section 2.3). The authors gave some information about the mechanism of this reaction, which passes through activated complexes and intermediates, in the order $[\text{SeI}_3\text{O}(\text{H}_2\text{O})_m]^\ddagger$, $\text{SeO}(\text{H}_2\text{O})_m$, $[\text{SeIOH}(\text{H}_2\text{O})_m]^\ddagger$, which clearly indicates the sequential replacement of oxygen by iodine. It is likely that the reaction continues with the formation of SeI_2 , which decomposed to Se^0 and I_2 , the final products of reaction 1.

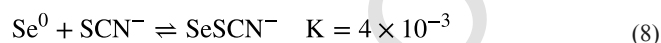
The aqueous phase reaction of selenous acid with thiocyanate gives the quite stable selenodithiocyanate, $\text{Se}(\text{SCN})_2$, as reported by Milne and Milne [35], who investigated the reaction of H_2SeO_3 with

HSCN by IR, Raman and ^{77}Se -, ^{13}C -, ^{15}N NMR spectroscopy:



Under stoichiometric conditions and selenous acid in the high millimolar range, selenium dithiocyanate slowly decomposes to elemental selenium at 0°C , over a period of hours.

Under analytical conditions (Se at trace or ultratrace level and $\text{SCN}^- \geq 0.1 \text{ mol L}^{-1}$), the elemental selenium which is formed is maintained in solution due to reaction [35]:



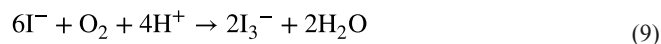
Reaction 7 passes through the formation of intermediates such as SeO_2SCN^- and $\text{SeO}(\text{SCN})_2$. Similarly to the reaction of selenous acid with iodide, the sequential replacement of oxygen atoms by thiocyanate brings to the formation of the final products SeX_2 ($\text{X}=\text{I}, \text{SCN}$), which is not stable in the case of iodide.

Dedicated CVG experiments were performed in order to evaluate the contribution of additive- Se^{IV} reaction on the generation of H_2Se . The results are reported in Fig. 4. The additives were allowed to react with Se^{IV} before reaction with THB, and the reaction times were varied from about 30 ms ($L_0=4 \mu\text{L}$) to 29 s ($L_0=3900 \mu\text{L}$). For $L_0=0 \mu\text{L}$ all the reagents are mixed at the same time and the reaction time is controlled by the rate of mixing of the solution, which is about 20 ms in this type of apparatus [5]. The results indicate that using a given concentration of iodide as the additive Se^{IV} is converted to Se^0 or to other non-reactive species which are formed in the reduction of Se^{IV} to Se^0 , with a rate that is dependent on acidity (Fig. 4a).

The fraction of Se^{IV} , α_{Se} which is present in solution at a given time can be estimated by Eq. (4) and the results are reported in Fig. 5, for different acidity of sample solution. These results give an indication of how fast the reduction of selenium is in the presence of iodide and can explain the dramatic drop of the relative absorbance signal, S/S_0 , that can be observed by increasing the reaction time from about 20 ms ($L_0=0 \mu\text{L}$) up to 29 s ($L_0=500 \mu\text{L}$) (Fig. 4a). The signal enhancement which is observed with 20 ms reaction time ($L_0=0 \mu\text{L}$) at acidity from 0.1 to 2.0 mol L^{-1} is the results of competitive reactions which can be described in the simplified reaction scheme 1:

Where the Se intermediate species could be similar to those discussed above (SeO , SeIOH , SeI_2 etc) and $\text{B}-\text{H}$ are hydridoboron or borane complex species which are formed in the same reaction conditions. The dramatic drop of generation efficiency from 2.0 to 5.0 mol L^{-1} acidity can be explained by assuming that the formation of Se^0 from Se intermediates is much faster than their reaction with hydridoboron species to form H_2Se .

The drop of sensitivity at 5 mol L^{-1} acidity could be also due to the oxidation of iodide by the dissolved oxygen (about $8.6 \times 10^{-3} \text{ mol L}^{-1}$ at 25°C) leading to formation of iodine,



which could deplete the concentration of THB. However, the rate of oxidation of iodide from dissolved oxygen is slow ($v=k [\text{O}_2][\text{I}^-][\text{H}^+]$, $k=1.38.6 \times 10^{-4} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ [36]) and it was not considered as a relevant reaction in the present continuous flow system.

In the case of thiocyanate its interaction with Se^{IV} produced a signal enhancement that is hardly dependent on both reaction time and acidity (Fig. 4b). This behavior is in agreement with the formation of stable selenium-thiocyanate complexes which are more reactive than

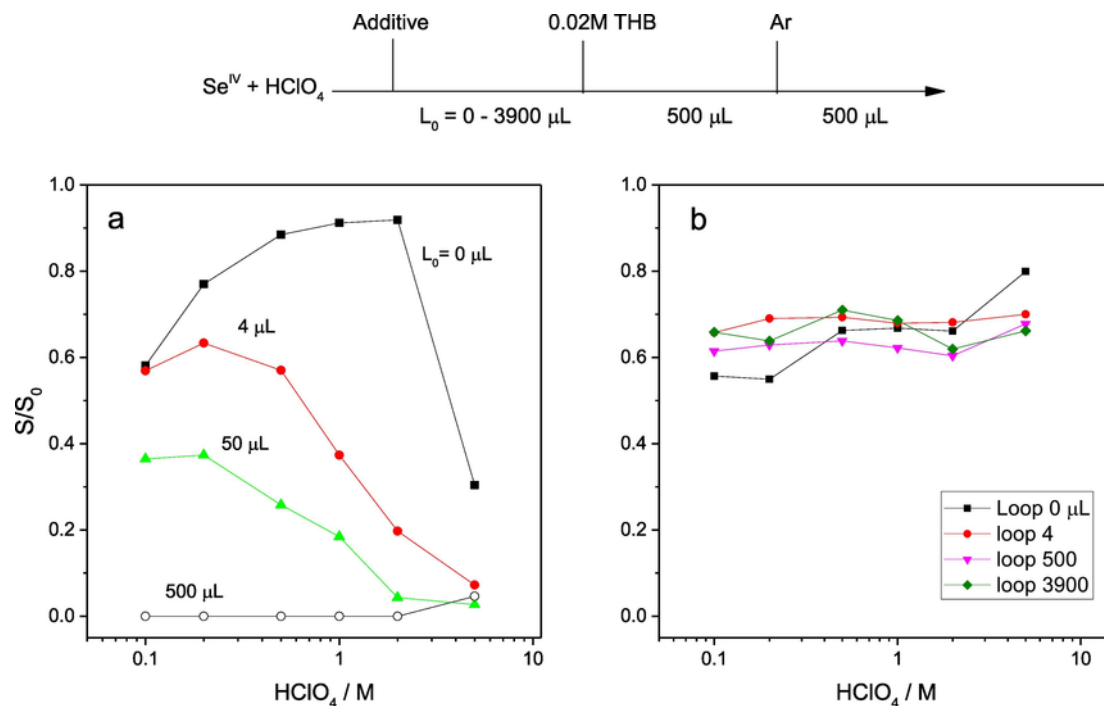


Fig. 4. Effect of sample acidity on the generation of H_2Se measured by CVG-AAS ($0.2 \mu\text{g mL}^{-1} Se^{IV}$) in the presence of additives using the delayed addition of THB to Se^{IV} -additive reaction mixture. (a) effect of iodide, 0.5 mol L^{-1} ; (b) effect of thiocyanate, 0.5 mol L^{-1} . Measurements at $L_0 = 0 \mu\text{L}$ were performed using chemifold setup B (Fig. 1); measurements at $L_0 \geq 4 \mu\text{L}$ were performed using chemifold setup C (Fig. 1); THB = 0.02 mol L^{-1} in $5 \times 10^{-3} \text{ mol L}^{-1} NaOH$.

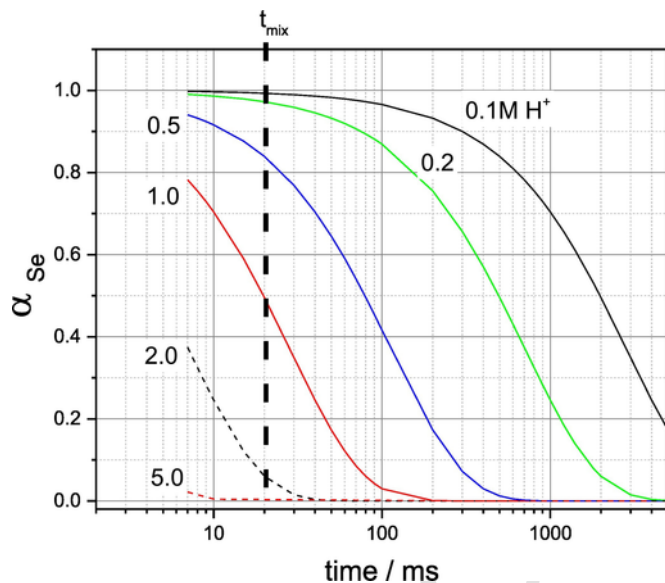


Fig. 5. Kinetics of Se^{IV} reduction by iodide calculated according to Eq. (4). α_{Se} is the fraction of Se^{IV} remaining in solution after a given reaction time. The calculations are made under conditions which are obtained after mixing equal volumes of 0.5 mol L^{-1} iodide solution with sample solution containing $0.2 \mu\text{g mL}^{-1} Se^{IV}$ at different acid concentrations (0.1, 0.2, 0.5, 1.0 and $2.0 \text{ mol L}^{-1} H^+$). t_{mix} is the approximate mixing time of solutions in the employed chemifold reactor.

H_2SeO_3 towards those borane species which are formed under the same reaction conditions. According to the studies of Milne and Milne [35] the reactive species could be one among the species SeO_2SCN^- , $SeO(SCN)_2$ and $Se(SCN)_2$. The formation of these stable selenium complexes of thiocyanate, can explain most of the signal enhancement observed in Fig. 2.

3.4. The effect of additive-borane complex formation on CVG of H_2Se

As discussed in Section 3.2, both iodide and thiocyanate perturb the hydrolysis rate of THB, indicating that these additives modify the mechanism of hydrolysis by forming intermediate hydridoboron species which are different from those formed in their absence. In this section we investigate the role that these additive-borane intermediates play in the enhancement of generation efficiency of H_2Se . The experiments consist of using the sequential mixing of the reagents using the chemifold setup B and C (Fig. 1). THB, with or without the additive, undergoes hydrolysis at different acidities and for different reaction times, the latter being controlled by the reaction loop volumes (0–500 μL). The hydridoboron species which are formed in the first loop are allowed to react with Se^{IV} in the next loop.

The results for iodide and thiocyanate are reported in Figs. 6 and 7, respectively. In both cases it is necessary to consider that also in the absence of additives some H_2Se has evolved because of the reactivity of the analytical substrate with hydridoboron species [7]. The net signal, that is the difference between the signal in the presence and in the absence of the additive, should be therefore considered in order to evaluate the contribution of the additive to signal enhancement. The net signals are reported in Figs. 6b and 7b for iodide and thiocyanate respectively.

In the case of iodide (Fig. 6b) here is clear contribution of signal enhancement due to formation of iodide-borane complexes passing from 0 to 50 μL reaction loop. Increasing further the hydrolysis time (500 μL , reaction time $< 5 \text{ s}$) led to signal decrease compared to both 0 and 50 μL reaction loop, indicating the loss of reactive iodide-borane complexes. This is also in agreement with the evidence that in the presence of iodide the hydrolysis rate of THB is enhanced, both at low and high acidities (Fig. 3). The dramatic drop of sensitivity at 5 mol L^{-1} acidity could be addressed both to the fast hydrolysis of io-

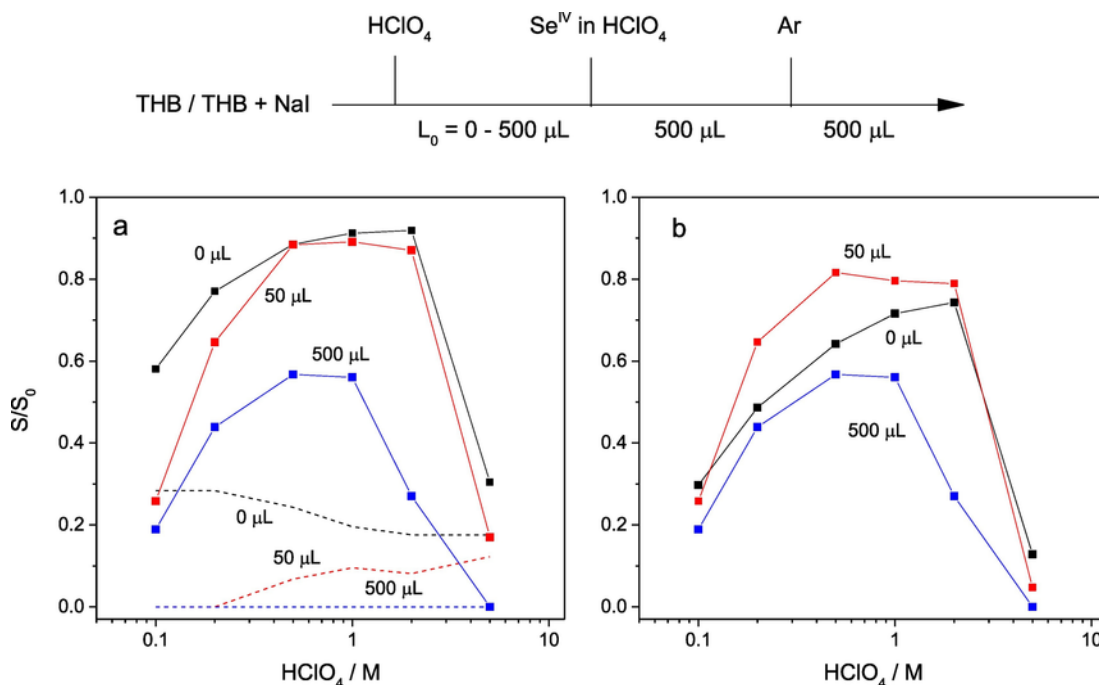


Fig. 6. (a) Effect of sample acidity on the generation of H_2Se , measured by CVG-AAS, using the delayed addition of Se^{IV} to NaI-acid-THB reaction mixture, with (solid line) and without (dashed line) NaI; (b) plot obtained by using the net signals obtained by difference of the signals reported in Fig. 6a in the presence of NaI (solid line) and in the absence of NaI (dashed line).

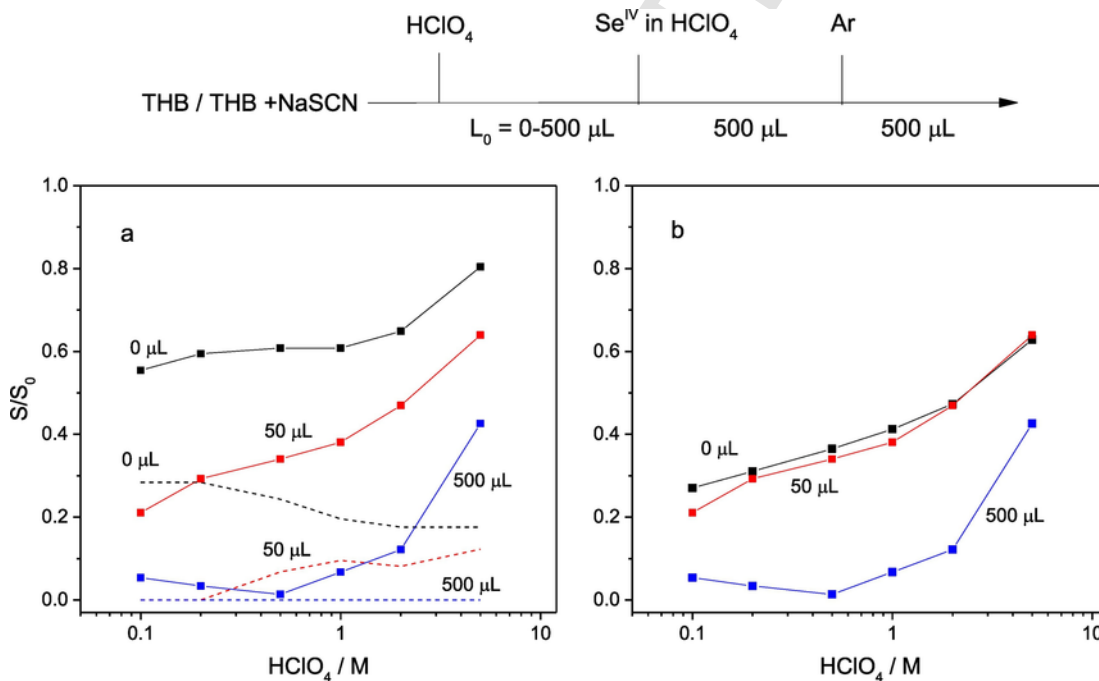


Fig. 7. (a) Effect of sample acidity on the generation of H_2Se , measured by CVG-AAS, using the delayed addition of Se^{IV} to NaSCN-acid-THB reaction mixture, with (solid line) and without (dashed line) NaSCN; (b) plot obtained by using the net signals obtained by difference of the signals reported in Fig. 1a in the presence of NaSCN (solid line) and in the absence of NaSCN (dashed line).

dide-borane complexes and also to the fast reduction of selenium by iodide according to the discussion of previous Section 3.3.

In the case of thiocyanate (Fig. 7b) there is no signal enhancement by following the formation of thiocyanate-borane species. In this case, at least in the range of acidities below $1 \text{ mol L}^{-1} \text{ HClO}_4$, the en-

hancement effect can be addressed to the formation of additive-selenium complexes. At higher acidities, it is likely that the formation of thiocyanate-borane complexes might contribute to the signal enhancement considering that this species are much more resistant than iodide-borane complexes to acid hydrolysis, as it is also confirmed by

the experiments reported in Fig. 3. The longer lifetime and the better reactivity of thiocyanate-borane and thiocyanate-selenium complexes compared to those complexes that are formed in the presence of iodide, are probably the reason for which at elevated acidities thiocyanate works much better than iodide.

3.5. Addition of NaI and NaSCN during Se^{IV} -THB reaction

The evidence reported in previous sections indicated that both iodide and thiocyanate can react with Se^{IV} species and THB/hydroboron species much faster than Se^{IV} species with THB/hydro-

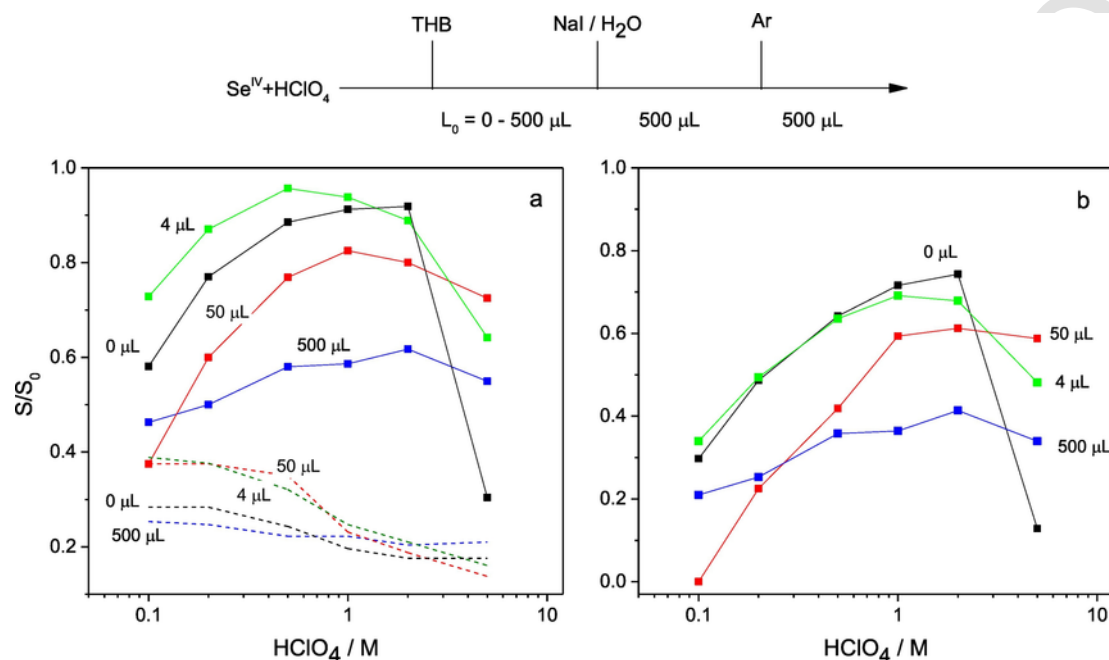


Fig. 8. (a) Effect of sample acidity on the generation of H_2Se , measured by CVG-AAS, using the delayed addition of NaI to Se^{IV} -acid-THB reaction mixture, with (solid line) and without (dashed line) NaI; (b) plot obtained by using the net signals obtained by difference of the signals reported in Fig. 8a in the presence of NaI (solid line) and in the absence of NaI (dashed line).

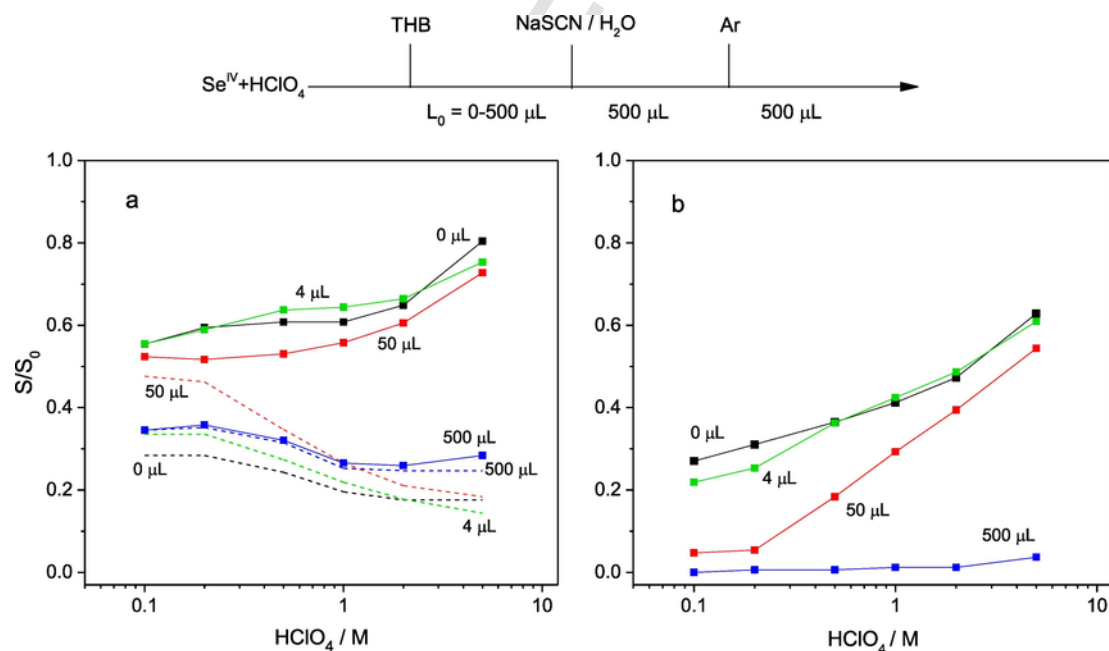
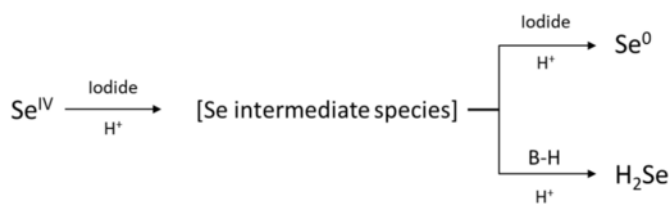


Fig. 9. (a) Effect of sample acidity on the generation of H_2Se , measured by CVG-AAS, using the delayed addition of NaSCN to Se^{IV} -acid-THB reaction mixture, with (solid line) and without (dashed line) NaSCN; (b) plot obtained by using the net signals obtained by difference of the signals reported in Fig. 9a, the presence of NaSCN (solid line) and in the absence of NaI (dashed line). Measurements at $L_0 = 0 \mu\text{L}$ were performed using chemifold setup B (Fig. 1); measurements at $L_0 \geq 4 \mu\text{L}$ were performed using chemifold setup C (Fig. 1). $\text{Se}^{\text{IV}} = 0.2 \mu\text{g mL}^{-1}$, $\text{NaSCN} = 0.5 \text{ mol L}^{-1}$, $\text{THB} = 0.02 \text{ mol L}^{-1}$ in $5 \times 10^{-3} \text{ mol L}^{-1}$ NaOH.



Scheme 1. – Simplified reaction scheme of CVG of H_2Se in the presence of iodide.

doboron species. In a series of experiments it was tested the effect of the delayed addition of the additive solution to the solution in which the reaction between H_2SeO_3 and THB has already started. The reaction times between Se^{IV} and THB are controlled by the volume of the loop L_0 (0–500 μL). The sequential mixing of the reagents was realized by using to the chemifold setup B and C (Fig. 1). The results are reported in Figs 8 and 9 respectively for iodide and thiocyanate. Also in this case, it is necessary to consider that in the absence of additives some H_2Se has evolved because of the reactivity of the analytical substrate with hydridoboron species [7]. The net signals which should be considered in order to evaluate the enhancement effect that can be addressed to the action of additives are reported in Fig. 8b and 9b for iodide and thiocyanate respectively.

Both thiocyanate and, in particular, iodide maintain their properties of increasing the yield of H_2Se generation when added soon after the starting of the reaction between Se^{IV} and THB. In this case the additive is added to a reaction solution which can contain, at the end of L_0 , selenium-borane complex intermediates [8] or selenium species which are intermediates between Se^{IV} and Se^{II} , in addition to unreacted Se^{IV} species and THB/hydridoboron species. The evidence that the generation efficiency of H_2Se is increased at the acidity of 5 mol L^{-1} using the delayed addition of iodide ($L_0 = 4\text{--}500 \mu\text{L}$, Fig. 8) indicates that the rate of reduction of selenium to H_2Se is higher than its rate of reduction to Se^0 . This effect cannot be produced by the reaction of iodide with both Se^{IV} and THB (Scheme 1) and can be

therefore addressed to the reaction of iodide with selenium-borane complex and/or selenium intermediates.

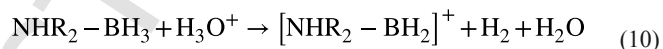
Thiocyanate (Fig. 9) appears to be noneffective when the time delay is increased ($L_0 = 500 \mu\text{L}$) but for the other conditions it maintains the properties to enhance the H_2Se generation efficiency at high acidities. For thiocyanate it cannot be excluded that also its reaction with selenium-borane complex and/or selenium intermediates can contribute to signal enhancement in addition to its reaction with Se^{IV} species and THB/hydridoboron species.

3.6. Effect of additives using amine boranes

As noted by Agterdenbos and Bax [26,27], the “catalytic effect” of iodide is not observed for arsenic-THB reaction system, as well as “catalytic effects” are not reported in the presence of either iodide or thiocyanate in the CVG of the other hydride forming elements [1]. In order to verify if this effect is peculiar of selenium-THB reaction system, it seemed therefore interesting to verify the effect of these additives on the generation of H_2Se by using borane reagents other than THB. Recently, both ammonia-borane (AB) and *tert*-butyl amine borane (TBAB) have proven to be effective reducing agents for the generation of H_2Se , using millimolar concentration of amine borane, in a wide range of acidities and using different type of acids [29].

Using $1.0 \text{ mol L}^{-1} \text{ HClO}_4$, both iodide and thiocyanate present a depressive effect on the generation of H_2Se , which is more pronounced for TBAB and using iodide (Fig. 10).

This result should be interpreted in the light of the mechanism of hydrolysis of amine boranes discussed recently. At high acidities ($\text{pH} < 0$) amine boranes decompose according to reaction:



In this case the interaction of the amine-borane cation and its derivatives with iodide or thiocyanate can lead to formation of additive-

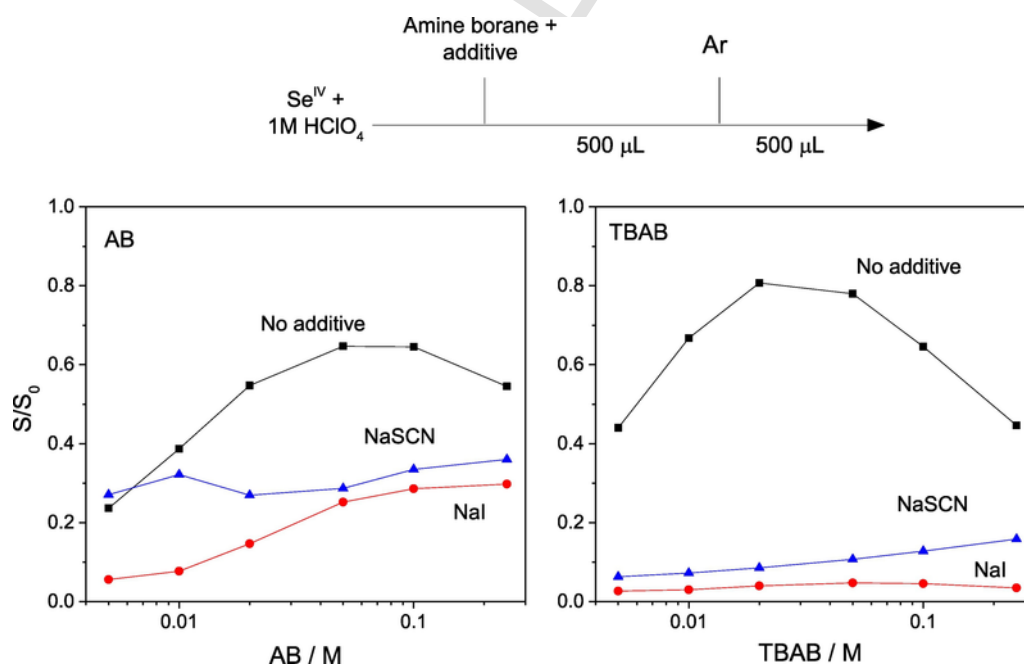


Fig. 10. CVG-AAS of H_2Se ($0.2 \mu\text{g mL}^{-1} \text{ Se}^{\text{IV}}$) by reduction with amine boranes observed in the absence or in the presence of additives: (a) Ammonia borane (AB); (b) *tert*Butylamine borane.

borane complexes, which are different from those formed with THB (Reaction 6), and they could be not reactive with those selenium species that are formed in the same reaction environment.

4. Conclusions

In CVG, the enhancement of generation efficiency of H_2Se produced by the presence of the additives iodide and thiocyanate, also termed “catalytic effect”, is clearly due to a modification of Se^{IV} -THB reaction system leading to a relative increase of the rate of formation of H_2Se compared to that of borane species. This effect seems to be peculiar of the Se^{IV} -THB reaction systems because no such a similar effect has been observed with different analytical substrates or, as reported here, with different borane reagents.

The modification of Se^{IV} -THB reaction system can occur through the formation of complexes of the additive with selenium species, borane species and selenium-borane complexes intermediates.

In the case of iodide most of its interactions with the species that are present in the reaction system seems to play a role in signal enhancement. The formation of divalent Se complexes of the type SeO , SeIOH , SeI_2 etc., which are the intermediates of the reduction $\text{Se}^{\text{IV}} \rightarrow \text{Se}^0$, contributes by forming Se-substrates which are more reactive than H_2SeO_3 , as well as the formation of species of the type $[\text{BH}_3\text{I}]^-$ contributes by generating borane species which are more reactive than hydridoboron species – $(\text{H}_2\text{O})\text{BH}_3$, $(\text{H}_2\text{O})_2\text{BH}_2^+$ etc. – towards the selenium substrates. At elevated acidities the reduction rate of $\text{Se}^{\text{IV}} \rightarrow \text{Se}^0$ produced by the iodide is much faster than the reduction rate of intermediate selenium substrates to H_2Se produced by borane species, leading to an almost complete signal suppression at 5.0 mol L^{-1} HClO_4 concentration. The $\text{Se}^{\text{IV}} \rightarrow \text{Se}^0$ reduction can be better controlled by the delayed addition of iodide to the Se^{IV} -THB reacting solution, which indicates that iodide can also reacts with selenium and selenium borane complex intermediates.

In the case of thiocyanate, the major contribution to signal enhancement can be addressed to the formation of additive-analyte complexes, SeO_2SCN^- , $\text{SeO}(\text{SCN})_2$, $\text{Se}(\text{SCN})_2$, rather than the formation of additive-borane complexes, $[\text{BH}_3\text{SCN}]^-$. The relative stability of both these additive complexes at elevated acidities produces the maximum signal enhancement, which can be achieved in the presence of thiocyanate as the additive. Also, the effectiveness of thiocyanate is partly maintained by its delayed addition to Se^{IV} -THB reacting solution at elevated acidities, but its reaction with selenium intermediates and/or selenium borane complex intermediates cannot be confirmed in the light of collected evidences.

References

- [1] J. Dedina, D.L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Wiley, Chichester, 1995.
- [2] P. Wu, L.A. He, C.B. Zheng, X.D. Hou, R.E. Sturgeon, Applications of chemical vapor generation in non-tetrahydroborate media to analytical atomic spectrometry, *J. Anal. At. Spectrom.* 25 (2010) 1217–1246.
- [3] R.E. Sturgeon, Z. Mester, Analytical applications of volatile metal derivatives, *Appl. Spectrosc.* 56 (2002) 202A–213A.
- [4] A. D'Ulivo, J. Dédina, Z. Mester, R.E. Sturgeon, B. Welz, Mechanisms of chemical generation of volatile hydrides for trace element determination (IUPAC technical report), *Pure Appl. Chem.* 83 (2011) 1283–1340.
- [5] A. D'Ulivo, C. Baiocchi, E. Pitzalis, M. Onor, R. Zamboni, Chemical vapour generation for atomic spectrometry. A contribution to the comprehension of reaction mechanisms in the generation of volatile hydrides using borane complexes, *Spectrochim. Acta B* 59 (2004) 471–486.
- [6] A. D'Ulivo, V. Loreti, M. Onor, E. Pitzalis, R. Zamboni, Chemical vapor generation atomic spectrometry using amine-boranes and cyanotrihydroborate(III) reagents, *Anal. Chem.* 75 (2003) 2591–2600.
- [7] A. D'Ulivo, M. Onor, E. Pitzalis, Role of hydroboron intermediates in the mechanism of chemical vapor generation in strongly acidic media, *Anal. Chem.* 76 (2004) 6342–6352.
- [8] A. D'Ulivo, Z. Mester, J. Meija, R.E. Sturgeon, Mechanism of generation of volatile hydrides of trace elements by aqueous tetrahydroborate (III), mass spectrometric studies on reaction products and intermediates, *Anal. Chem.* 79 (2007) 3008–3015.
- [9] M. Welna, W. Zyrnicki, Investigation of simultaneous generation of arsenic, bismuth and antimony hydrides using inductively coupled plasma optical emission spectrometry, *Anal. Lett.* 44 (2011) 942–953.
- [10] E. Pitzalis, M. Onor, M.C. Mascherpa, G. Pacchi, Z. Mester, A. D'Ulivo, Chemical generation of arsane and methylarsanes with amine boranes. Potentialities for nonchromatographic speciation of arsenic, *Anal. Chem.* 86 (2014) 1599–1607.
- [11] A. D'Ulivo, Chemical vapor generation by tetrahydroborate(III) and other borane complexes in aqueous media. A critical discussion of fundamental processes and mechanisms involved in reagent decomposition and hydride formation, *Spectrochim. Acta B* 59 (2004) 793–825.
- [12] A. D'Ulivo, Mechanism of generation of volatile species by aqueous boranes. Towards the clarification of most controversial aspects, *Spectrochim. Acta B* 65 (2010) 360–375.
- [13] A. D'Ulivo, Mechanisms of chemical vapor generation by aqueous tetrahydroborate. Recent developments toward the definition of a more general reaction model, *Spectrochim. Acta B* 119 (2016) 91–107.
- [14] I.D. Brindle, X.-C. Le, Reduction of interferences in the determination of germanium by hydride generation and atomic emission spectrometry, *Anal. Chim. Acta* 229 (1990) 239–247.
- [15] H. Chen, I.D. Brindle, X.-C. Le, Prereduction of arsenic(V) to Arsenic(III), enhancement of the signal, and reduction of interferences by L-cysteine in the determination of arsenic by hydride generation, *Anal. Chem.* 64 (1992) 667–672.
- [16] E. Pitzalis, D. Ajala, M. Onor, R. Zamboni, A. D'Ulivo, Chemical vapor generation of arsane in the presence of L-cysteine. Mechanistic studies and their analytical feedback, *Anal. Chem.* 79 (2007) 6324–6333.
- [17] E. Pitzalis, M.C. Mascherpa, M. Onor, A. D'Ulivo, Mechanisms involved in stannane generation by aqueous tetrahydroborate(III). Role of acidity and L-cysteine, *Spectrochim. Acta B* 64 (2009) 309–314.
- [18] J.R. Castillo, J.M. Mir, C. Martinez, J. Val, M.P. Colón, Influence of oxidizing agents in lead determination by hydride generation direct flame atomic absorption spectroscopy, *Mikrochim. Acta* 85 (1985) 253–263.
- [19] C. Nerin, S. Olavide, J. Cacho, A. Garmica, Determination of lead in airborne particulate by hydride generation, *Water Air Soil Pollut.* 44 (1989) 339–345.
- [20] A. D'Ulivo, M. Onor, R. Spiniello, E. Pitzalis, Mechanisms involved in chemical vapor generation by aqueous tetrahydroborate(III) derivatization. Role of hexacyanoferrate(III) in plumbane generation, *Spectrochim. Acta B* 63 (2008) 835–842.
- [21] B. Deng, X. Xu, Y. Xiao, P. Zhu, Y. Wang, Understanding the effects of potassium ferricyanide on lead hydride formation in tetrahydroborate system and its application of lead in milk using hydride generation inductively coupled plasma optical emission spectrometry, *Anal. Chim. Acta* 853 (2014) 179–186.
- [22] A. D'Ulivo, Comment on “understanding the effects of potassium ferricyanide on lead hydride formation in tetrahydroborate system and its application of lead in milk using hydride generation inductively coupled plasma optical emission spectrometry” by B. Deng, X. Xu, Y. Xiao, P. Zhu, Y. Wang, *Anal. Chim. Acta* 884 (2015) 26–27.
- [23] B. Deng, X. Xu, Y. Xiao, P. Zhu, Y. Wang, Response to “comment on understanding the effects of potassium ferricyanide on lead hydride formation in tetrahydroborate system and its application of lead in milk using hydride generation inductively coupled plasma optical emission spectrometry” by Alessandro D'Ulivo, *Anal. Chim. Acta* 884 (2015) 28.
- [24] A. D'Ulivo, S.S.T. Battistini, E. Pitzalis, R. Zamboni, Z. Mester, R.E. Sturgeon, Effect of additives on the chemical vapour generation of bismuthane by tetrahydroborate(III) derivatization, *Anal. Bioanal. Chem.* 388 (2007) 783–791.
- [25] J. Agterdenbos, J.T. van Elteren, D. Bax, J.P. Ter Heege, The determination of selenium with hydride generation AAS - IV, Application to coal analysis. *Spectrochim. Acta, Part B* 41 (1986) 303–316.
- [26] J. Agterdenbos, D. Bax, A study on the generation of hydrogen selenide and decomposition of tetrahydroborate in hydride generation atomic absorption spectrometry, *Anal. Chim. Acta* 188 (1986) 127–135.
- [27] J. Agterdenbos, D. Bax, Mechanisms in hydride generation AAS, *Fresenius, Z. Anal. Chem.* 323 (1986) 783–787.
- [28] A. D'Ulivo, L. Gianfranceschi, L. Lampugnani, R. Zamboni, Masking agents in the determination of selenium by hydride generation technique, *Spectrochim. Acta B* 57 (2002) 2081–2094.
- [29] L. D'Ulivo, R. Spiniello, M. Onor, B. Campanella, Z. Mester, A. D'Ulivo, Behavior and kinetic of hydrolysis of amine boranes in acid media employed in chemical vapor generation, *Anal. Chim. Acta* 998 (2018) 28–36.
- [30] J.A. Neptune, E.L. King, The rate law for the reaction of selenous acid and iodide ion, *J. Am. Chem. Soc.* 75 (1953) 3069–3072.

- [31] J.S. Cha, Thirty six years of research on the selective reduction and hydroboration, *Bull. Kor. Chem. Soc.* 32 (2011) 1808–1846.
- [32] V.D. Aftandillian, H.C. Miller, E.L. Muetterties, Chemistry of boranes. I – reactions of boron hydrides with metal and amine salts, *J. Am. Chem. Soc.* 83 (1961) 2471–2474.
- [33] K. Nozaki, Y. Aramaki, M. Yamashita, S. Ueng, M. Malacria, E. Lacôte, D.P. Curran, Boryltrihydroborate: synthesis, structure, and reactivity as a reductant in ionic, organometallic, and radical reactions (in supporting information), *J. Am. Chem. Soc.* 132 (2010) 11449–11451.
- [34] B.C. Hui, Synthesis and properties of borohydride derivatives, *Inorg. Chem.* 19 (1980) 3185–3186.
- [35] C. Milne, J. Milne, Studies on the interaction of selenite and selenium with sulphur donors. Part 5. thiocyanate, *Can. J. Chem.* 74 (1996) 1889–1895.
- [36] G. Schmitz, Iodine oxidation by hydrogen peroxide in acidic solutions, Bray-Liebhaufsky reaction and other related reactions, *Phys. Chem. Chem. Phys.* 12 (2010) 6605–6615.