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Managing transition metal interferences during chemical vapor generation using the hydrolysis products of tetrahydridoborate: a proof-of-concept study†

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The negative impact of liquid phase interferences of transition metals has plagued chemical vapor generation with tetrahydridoborate since its introduction, which was more than fifty years ago. Herein, the interference from selected transition metal ions in the generation of SbH_3 and BiH_3 was investigated using the hydrolysis products of $NaBH_4$-hydridoboron intermediates (BH)-as derivatization reagents instead of $NaBH_4$. The BH intermediates were simply generated on-line in a pre-hydrolysis coil of the instrumental set-up. Compared to $NaBH_4$, the use of BH intermediates allowed for significantly improved tolerance to the interference of Ni(II), Co(II), and Cu(II) (tolerance limit of ≥ 100 mg L^{-1}) for Bi and Sb determination in the absence of any masking agents and in a wide range of acidity. Their applicability to real complex samples was successfully demonstrated by the determination of Sb and Bi in steel and copper standard reference materials. Beyond the analytical application, this work aims to play a part in the comprehension of borohydride chemical behaviour, which is still not completely understood.

During the chemical vapor generation (CVG) of volatile hydrides with aqueous tetrahydridoborate (THB) (MBH_4, M = Na or K), major problems arise from interference caused by the presence of foreign species, mainly transition metals.[1,2]
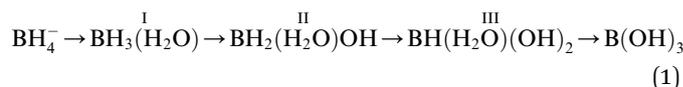
One of the tedious interference mechanisms is the capture of the generated hydride on the surface of metal/metal boride nanoparticles, which are formed by the reaction of THB with metal ions,[4,5] but other mechanisms can also contribute to interference, such as the formation of insoluble products[4] and the catalytic decomposition of THB by metal/metal boride nanoparticles.[6]

Interferences can be kept under control by sample dilution,[1] the careful optimization of acidity and reductant

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concentration,[4,7] and minimizing the contact time between the generated hydride and the solution.[1] The most effective tool for interference control is the use of masking agents, for example, L-cysteine[8–11] and thiourea.[10,12] In worst cases, when none of the mentioned approaches is effective, the only alternative is the adoption of separation methods (precipitation, coprecipitation, ion-exchange chromatography, and others), which are time-consuming and prone to the risk of analyte losses and sample contamination.[1]

Amine boranes for the CVG of hydride forming elements clearly demonstrated that for some elements, such as As(III), Sb(III), and Bi(III), the tolerance limit (*i.e.* the concentration of an interferent, which changes the observed characteristics of the analyte signal by 10%)[13] to interference from Ni(II), Co(II), and Cu(II) can be improved up to 500 times compared to that of THB. This behaviour can be addressed by the fact that amine boranes are milder hydride reagents than THB. This is also confirmed by their much more pronounced resistance to hydrolysis.[3]

The stepwise hydrolysis products of THB in mild acidic media (pH = 1–6) can be simplified using the following scheme:[14]

$$BH_4^- \rightarrow \overset{I}{BH_3}(H_2O) \rightarrow \overset{II}{BH_2}(H_2O)OH \rightarrow \overset{III}{BH}(H_2O)(OH)_2 \rightarrow B(OH)_3 \quad (1)$$

where the intermediate hydridoborate species I, II, and III are more resistant to hydrolysis than THB itself. In particular, hydrolysis rates of species II and III are acid-independent.[23]

According to the above-discussed evidence for amine boranes, it seems worthwhile to verify whether the milder borane species intermediates arising from the hydrolysis of THB (species I, II, and III) could also be useful for interference control. Specifically, here, we propose that the hydridoboron intermediates (BH) are more selective and less reactive in the generation of volatile hydrides in the presence of transition metals. To test our hypothesis, Sb(III) and Bi(III) were selected as model analytes because they efficiently generate SbH_3 and BiH_3

following the reaction with BH intermediates over a wide range of acidity.[15]

The results on the effectiveness of BH intermediates in interference control are interesting and could be extended to other analytes whenever the CVG of the volatile species can be efficiently achieved using BH intermediates as the derivatization reagents.

To verify the hypothesis that the BH intermediates react more selectively than THB with the analytical species (Sb(III) and Bi(III)) in the presence of transition metal interferences, the adopted experimental setup allowed the reaction of the analytes with the different BH species formed during the acid decomposition of THB. Hydrochloric acid was used in the experiments, considering its widespread use in CVG and the almost ineffective role of the chloride anion in the process. THB was

hydrolysed with $0.01–5$ mol L^{-1} HCl by the reaction in a coil having a fixed volume ($0–0.1–0.5–1$ mL), using the mixing sequence reported in Fig. S1B. Fig. S2† shows preliminary experiments where the reactivity of BH intermediates towards the selected analytes in the absence of interference was investigated. According to the behaviour of each analyte, working with the three hydrolysis coils, we selected four HCl concentrations (i.e., $0.1, 0.5, 1,$ and 2 mol L^{-1}) for the subsequent experiments.

The role of BH intermediates in mitigating the chemical interferences from the transition metals, i.e. Fe(III), Fe(II), Ni(II), Co(II), and Cu(II) was then investigated. Preliminary experiments conducted at three concentration levels for each interfering species ($1–10–100$ mg L^{-1}) showed that 100 mg L^{-1} corresponds to the concentration of M^{n+} causing a significant signal loss
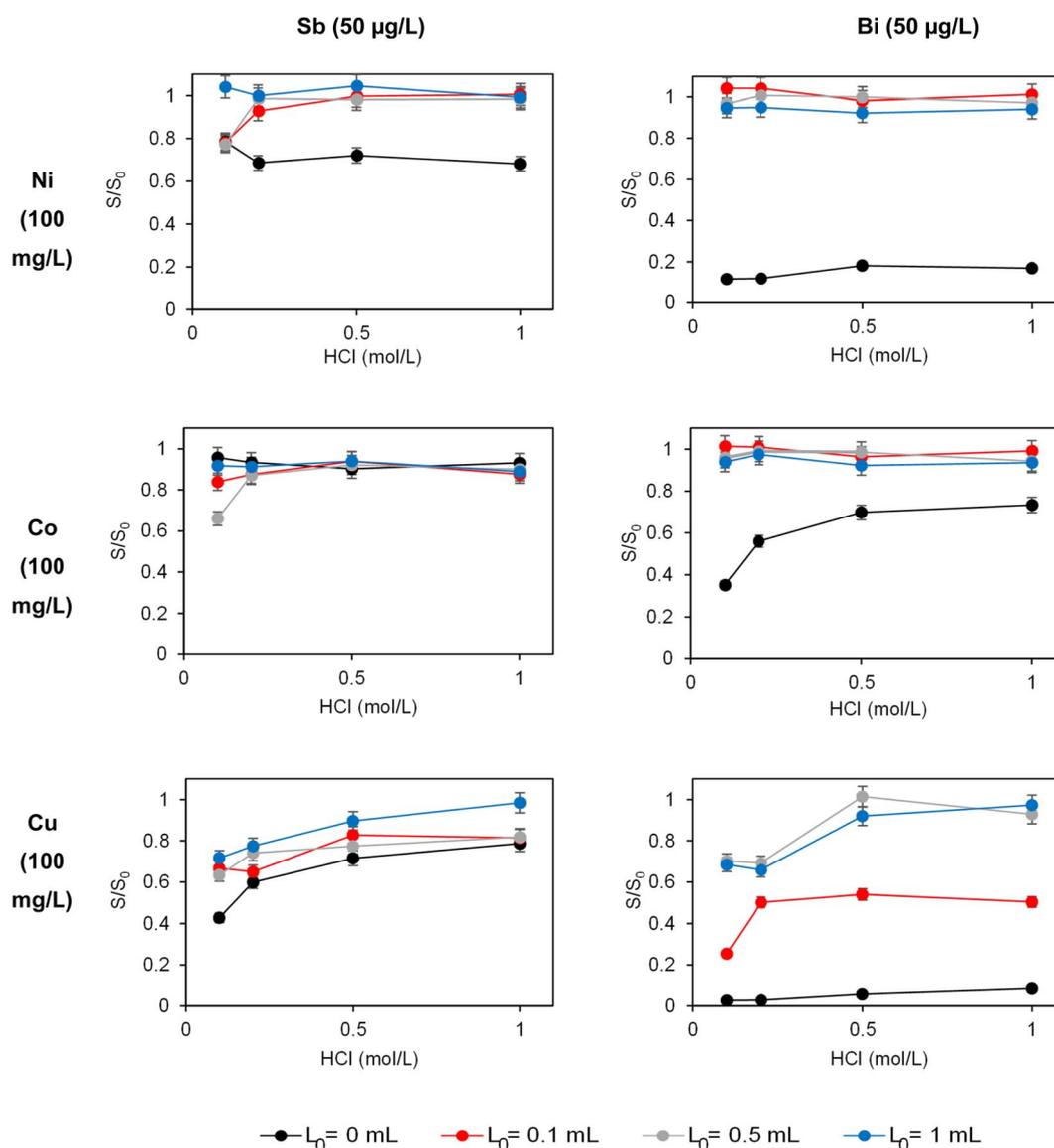

Fig. 1 FI-CVG-AFS experiments for 50 µg L^{-1} Sb (left panel) and Bi (right panel) in the presence of 100 mg L^{-1} Ni, Co, and Cu using the mixing sequences reported in Fig. S1B.† The reference signal S_0 was obtained with the configuration reported in Fig. S1A;† 1 mol L^{-1} HCl and 1% THB. The confidence interval was calculated at 95% from the mean of 3 replicates.

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(>10%) when working with the no-hydrolysis configuration (Fig. S1A†). This value was then selected for the subsequent experiments. Iron was not further investigated, as it does not significantly interfere with the detection of Sb and Bi even at 1000 mg L^{-1}.

The in-house built 5-way mixing block (Fig. S1A†) enabled a significant reduction of the effect of interfering species by keeping at a minimum the contact time between THB, E^{m+}, and M^{n+}. Indeed, with respect to a traditional configuration where a 3-way mixing block (E^{m+} + M^{n+} − THB − HCl) is usually connected to a reaction coil followed by Ar stripping, we observed that the signal degradation due to the presence of interference is less critical.

Fig. 1 shows the effect of THB hydrolysis (experimental configuration in Fig. S1B†) over the interferences due to 100 mg L^{-1} Ni(II), Co(II), and Cu(II). The selectivity of the BH intermediates with respect to the analytes is particularly clear for Bi(III). Without hydrolysis, the decrease in the Bi(III) AFS signal is almost 100% in the presence of 100 mg L^{-1} of Ni and Cu and between 30 and 65% in the presence of 100 mg L^{-1} of Co, but the use of BH intermediates enabled working in large excess of transition metals (1 : 2000) without significant signal loss, and in most case even at low acidity values. In the presence of Cu, which represents one of the most challenging element in CVG, the BiH$_3$ signal increases from 5 to 10% up to 90 to 100% (with respect to the reference signal under optimal conditions) working at 0.5–1 mol L^{-1} HCl and L_0 = 0.5–1 mL. It is worth underlining that the tolerance limits for Cu in CVG of BiH$_3$ previously reported (in 1 mol L^{-1} HCl reaction media) were 0.2, 2, and 100 mg L^{-1} using THB, BH$_3$·NH$_3$ (AB), and BH$_3$·tert-butylNH$_2$ (TBAB), respectively.[16]

Despite Sb(III) being characterized by a higher resistance to interference from transition metals, irrespective of the instrumental configuration or HCl concentration (see Fig. 1), the same trend as Bi(III) was observed: Cu^{2+} > Ni^{2+} > Co^{2+}. For Sb(III), the best result was obtained at 1 mol L^{-1} HCl and L_0 = 1 mL, where the recovery of SbH$_3$ goes from 88% in the presence of 100 mg L^{-1} Co^{2+} up to 100% in the presence of 100 mg L^{-1} Cu^{2+} and Ni^{2+}.

It is interesting to note from Fig. 1 that the use of BH intermediates allows, in general, good control of interferences at low sample acidity values, conditions which generally enhance the interference effects in CVG with THB.[1]

Among the causes that contribute to the reduction of interferences when CVG is performed with BH intermediates, there is certainly the lower formation of metal/metal boride nanoparticles. This effect is evidenced by the fact that the surfaces of the reaction system are covered more slowly by interference products than when THB is used. Thus, the use of BH intermediates mitigates both direct and memory interferences in the liquid phase.

The presence of transition metals at high concentrations in environmental or industrial samples could limit the application of CVG to the quantification of relevant analytes. The analytical benefits of working with BH intermediates are demonstrated against the determination of Sb and Bi in challenging matrices: two standard reference materials of steel (SRM-662 and SRM-663) and one of copper (SRM-399), which were dissolved according to the procedure described in the experimental section.

The compositions of the three SRMs are reported in Table 1. Steel SRMs are characterized also by the presence of Cr, V, and Mo and for this reason, the combined effect of these three elements on BiH$_3$ and SbH$_3$ generation was evaluated. A mixture of Cr(III), V(IV), and Mo(VII), reflecting the ratios commonly found in steel samples (75 mg L^{-1} Cr, 15 mg L^{-1} V, and 15 mg L^{-1} Mo), was added to 50 μg L^{-1} of Bi(III) or Sb(III), and the solutions were analyzed with the configurations shown in Fig. S1A and B.† The results show that Cr/V/Mo does not significantly interfere in the determination of Bi even without the pre-hydrolysis of THB. For Sb(III) the relative signal (S/S_0) increased from 55% (no-hydrolysis setup) to 72% (1 mL hydrolysis coil, 0.2 M HCl), as shown in Fig. S3.†

For the determination of Sb and Bi in the SRMs, THB hydrolysis conditions were selected on the basis of the results discussed above. The results are displayed in Fig. 2. When BH intermediates were used, the observed values for Bi were statistically equivalent to those certified. In contrast, the traditional configuration (even though the 5-way mixing block reduces the contact time between the formed hydrides and the metals) did not allow accurate determination of Bi, especially in SRM-399 where the interference from copper was more pronounced. As regards the determination of Sb in steel samples, the concentration values obtained through the instrumental configuration optimized for the hydrolysis of THB fall within the range declared by the manufacturer.

Table 1 Elemental composition of the three CRMs analyzed in this work

	Sb (%)	Bi (%)	Pb (%)	Co (%)	Ni (%)	Cu (%)	Cr (%)	V (%)	Mo (%)	Fe (%)
SRM-662	0.012 ± 0.001	0.002^a	—	0.3	0.6	0.51	0.3	0.04	0.07	95.3
SRM-663	0.002 ± 0.001	0.0008^a	0.0022 ± 0.0001	0.048	0.32	0.098	1.31	0.31	0.03	99.4

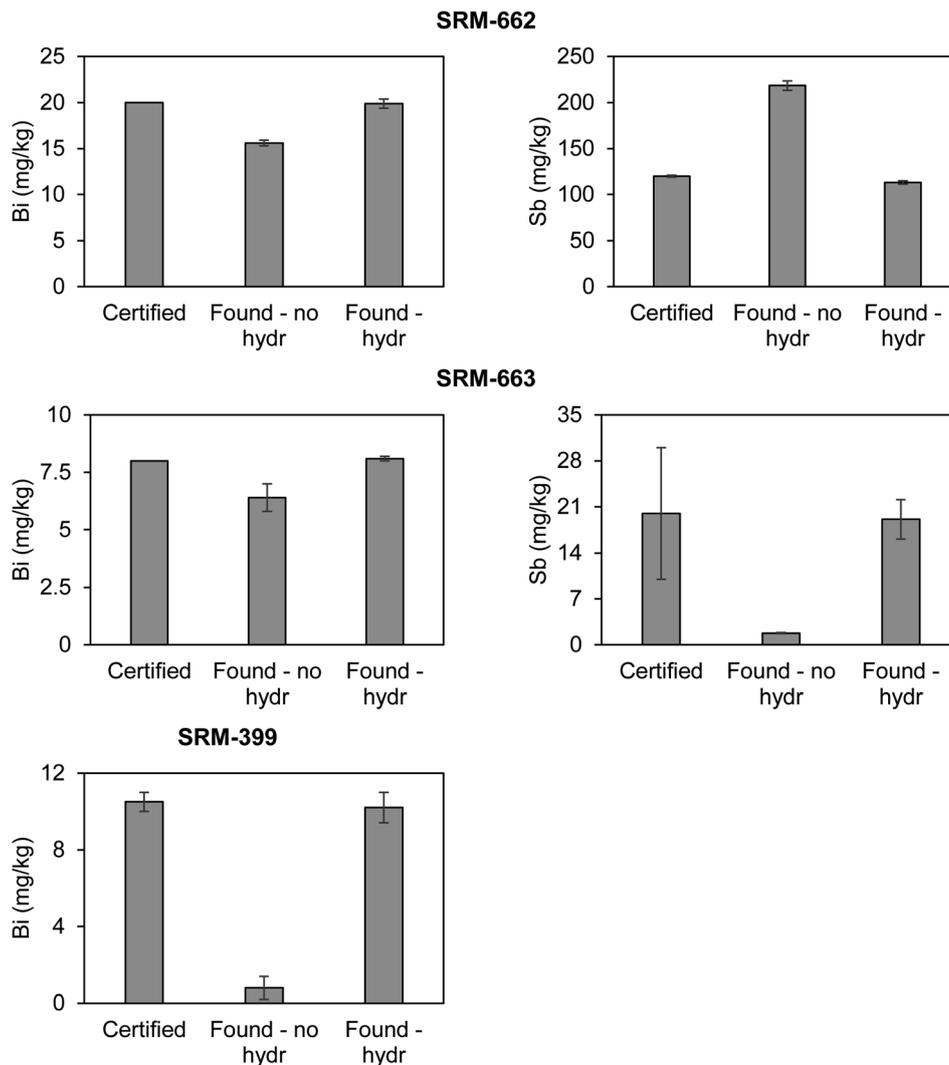|	Sb (mg kg^{-1})	Bi (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Cu (%)
SRM-399	30 ± 5	10.5 ± 0.5	0.5	506	99.79

^{a} Information value only.

Fig. 2 Comparison of the results for Bi (left panel) and Sb (right panel) determination in the SRM with the traditional configuration (Fig. S1A†) and THB hydrolysis configuration (Fig. S1B†).

Interestingly, for SRM-662 the concentration of Sb found with the no-hydrolysis configuration was significantly higher than the certified value (*i.e.*, 188%) whereas for SRM-663 only 13% of Sb with respect to the certified value was recovered (see Fig. 2). Antimony was not quantified in SRM-399 since the oxidative digestion protocol, necessary for the treatment of copper ores, resulted in the conversion of all Sb species to Sb(v) from which SbH$_3$ could not be generated with the same efficiency as from Sb(III). We avoided the use of the pre-reducing agents (KI, L-cysteine, thiourea, *etc.*) since they also act as masking agents, thus avoiding the evaluation of the sole effect of BH intermediates in the control of interferences.

In conclusion, through this communication, we demonstrated that in the CVG of Sb and Bi volatile hydrides, the interference arising from transition metals (Ni, Co, Cu, V, Cr, Mo) can be easily kept under control by replacing the THB reagent with the intermediate BHs that are formed from its hydrolysis. This strategy is feasible because for these elements the generation efficiency of the corresponding hydrides is not significantly depleted by replacing THB with BH intermediates (see Fig. S2†). The best BH intermediates are those giving no or minimal losses of analytical sensitivity coupled with a significant increase of tolerance towards the selected interfering metals. BH intermediates were easily generated online by varying the sample acidity (from 0.1 to 1.0 mol L^{-1} HCl) and the time of hydrolysis (reaction coil volume 0.1–1.0 mL) of THB. Interferences are completely eliminated up to the maximum tested concentration of 100 mg L^{-1} and in many cases even at low sample acidity values, where interferences are particularly severe using THB.

The reported results clearly indicate that BH intermediates are more selective towards the analytical substrate than the interfering metal ions. This feature shows a novel side of THB reactivity, which allows perspective to avoid the use of masking agents for the interference control as demonstrated by the application of the proposed procedure to determine trace Sb and Bi in metallurgical samples standard reference materials.

The use of a BH intermediate, BH_3OH^-, synthesized online,[17] has been applied to the CVG of Cd[18] and to the reduction of several organic substrates in synthesis and catalysis.[19–22] The intermediate BH_3OH^- has a reducing power, which is the intermediate between $NaBH_4$ and the powerful $LiAlH_4$.[22] The strategy proposed in the present work could be of more general interest in all those applications where milder reducing agents, more selective than THB reagent, are required for the reduction of both inorganic and organic substrates.

Author contributions

Conceptualization and methodology: BC, AD; experimental analysis: MB, MO, BC. Writing – original draft: BC. Writing – review and editing: BC, AD, MO, EP. Data curation: MB, BC. Supervision: BC, AD.

Conflicts of interest

There are no conflicts to declare.

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