

## SUPPORTING INFORMATION TO

### **How to manage transition metal interferences in chemical vapor generation by using the hydrolysis products of tetrahydridoborate: a proof of concept study**

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## Materials and methods

**Chemicals.** Sodium tetrahydridoborate, powder,  $\geq 98.0\%$  (Sigma Aldrich). Sodium hydroxide (NaOH), 30%, TraceSELECT (Fluka). Hydrochloric acid (HCl), 37%, ACS reagent (Sigma Aldrich). Copper(II) chloride, nickel(II) chloride, cobalt(II) chloride (Carlo Erba). Iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate (Sigma Aldrich). Stock solutions of vanadium(IV), chromium(III) and molybdenum(VII) at  $1000 \text{ mg L}^{-1}$  (Fluka).

Working solutions of THB were prepared freshly and stabilized with NaOH ( $0.1 \text{ mol L}^{-1}$ , unless otherwise specified). Solutions were clear and colourless and did not require filtration. Working solutions of Bi(III) and Sb(III) were prepared from serial dilution of commercial stock solutions ( $1000 \text{ mg L}^{-1}$  in 2%  $\text{HNO}_3$ , Fluka) with HCl. Stock solutions of transition metals at  $1000 \text{ mg L}^{-1}$  in water were prepared from the corresponding chloride. For Cr, V and Mo a mixed solution in water was prepared respectively at  $75 - 15 - 15 \text{ mg L}^{-1}$ .

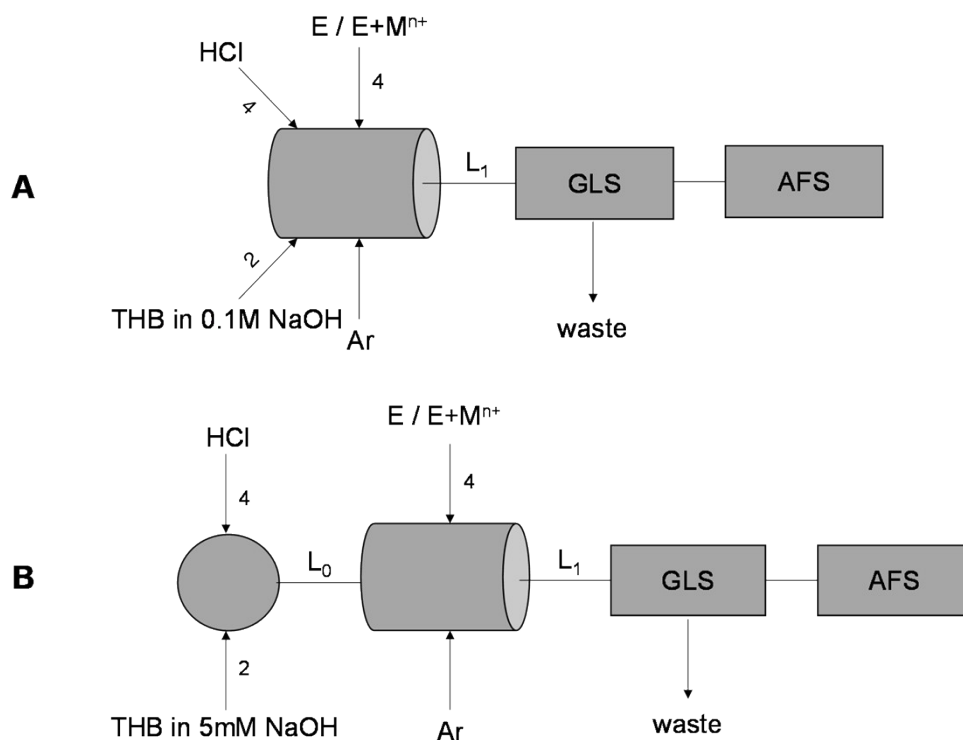
All the other chemicals were analytical grade reagents or higher. Ultra-pure water purified by using a Purelab Pro (USF,  $\rho = 18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) system was used in all the experiments.

**Apparatus.** A laboratory assembled atomic fluorescence spectrometer (AFS) was employed for the experiments. The AFS apparatus was described elsewhere.<sup>1</sup> A miniature Ar–H<sub>2</sub> diffusion flame ( $130 \text{ mL min}^{-1}$  Ar,  $80 \text{ mL min}^{-1}$  H<sub>2</sub>) supported on an 8 mm quartz tube was used as an atomizer for AFS measurements. Commercially available radiation sources (Sb and As electrodeless discharge lamp - EDL System 2 by Perkin-Elmer and Bi electrodeless discharge lamp by IST - Imaging & Sensing Technology) were used.

**Chemical vapor generation.** Flow injection CVG (FI-CVG) experiments were carried out using a HPLC pump (Dionex IP20) and a six-ways injection valve (Rheodyne, RH7725I) fitted with a  $100 \mu\text{L}$  sample coil. Ismatec Tygon microtubings of appropriate diameters were used with peristaltic pumps (Cole-Parmer Masterflex; Ismatec Reglo) for propelling the analyte and reductant and for the removal of waste solutions from the gas–liquid separator (GLS). Unless otherwise specified, reagent flow rates were  $4 \text{ mL min}^{-1}$  for the sample or blank, and  $2 \text{ mL min}^{-1}$  for THB solutions. The gas–liquid mixture leaving the chemifold was directly delivered to the GLS (60 mm long, 10 mm i.d., borosilicate glass) through a short transfer channel (about  $50 \mu\text{L}$  volume), which was obtained by connecting the mixing block to the GLS inlet with the aid of PTFE fittings (Bola, Germany). The gaseous products leaving the GLS were delivered to the atomizer by a PFA tube (30 cm long, 3 mm o.d., 1 mm i.d.).

Depending on experiments, different chemifolds were assembled in such a way as to be able to vary the mixing sequence and the reaction times of the reagents (see Figure 1). This was accomplished

using various combination of T-junctions (3-way mixing block, Kel-F, 0.8 mm i.d. channels, Ismatec), a custom made 5-way mixing block (Kel-F, 0.8 mm i.d. channels)<sup>2</sup>, and mixing/reaction coils (Teflon PFA, 0.5–0.8 mm i.d.) of various volumes (from 0.1 to 1 mL).



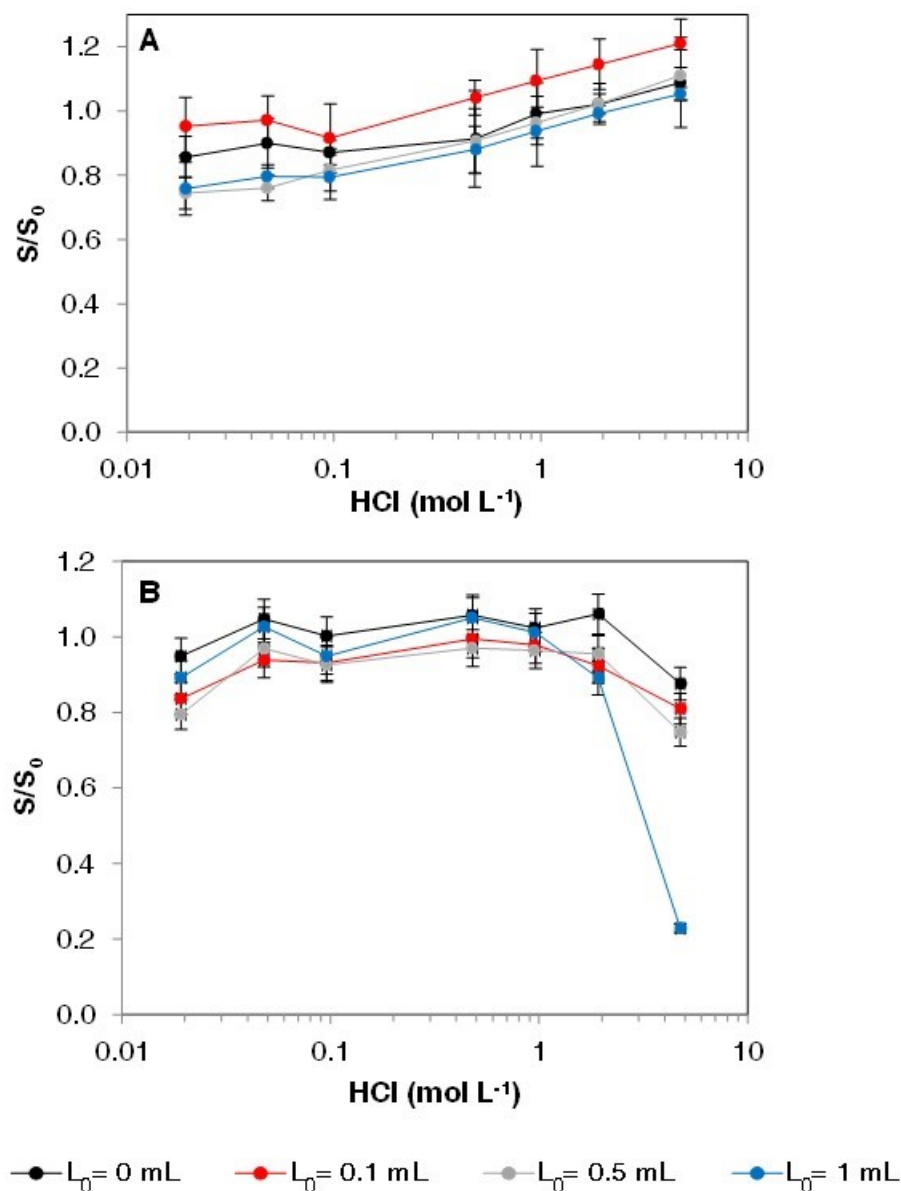
**Figure S1.** Schematic representation of the chemifold setups used for the sequential addition of reagents. Numbers represent solution flow-rates in  $\text{mL min}^{-1}$ . The volume of reaction coil  $L_0$  varied from 0.1 to 1 mL,  $L_1 = 50 \mu\text{L}$ . Concentration of reagents: A) 1%  $\text{NaBH}_4$  in  $0.1 \text{ mol L}^{-1}$   $\text{NaOH}$ ; B) 1%  $\text{NaBH}_4$  in  $5 \text{ mmol L}^{-1}$   $\text{NaOH}$ . Ar flow rate was set at  $180 \text{ mL min}^{-1}$ . Analyte (E) concentration was  $50 \mu\text{g L}^{-1}$ , transition metals concentration ( $\text{M}^{n+}$ ) was varied between 1 and  $100 \text{ mg L}^{-1}$ .

**Standard reference materials.** The feasibility of the analytical procedure described in this work was verified using three Standard Reference Material (SRM) supplied by the National Institute of Standards and Technology (NIST): SRM 662 (AISI 94B17 Steel), SRM 663 (Chromium-Vanadium Steel) and SRM 399 (Unalloyed copper). The selected protocol for preparation of SRM 662 and 663 consists of mild acid digestion of approximately 0.1 g of sample with 2 mL of  $5 \text{ mol L}^{-1}$   $\text{HCl}$ . The samples were heated on a hot plate at  $70^\circ\text{C}$  for three hours, then 0.2 mL of 37%  $\text{HCl}$  were added and the heating was continued until completed sample dissolution. SRM 399 (approximately 0.1 g) was digested with 3 mL of 65%  $\text{HNO}_3$  and 1 mL of 37%  $\text{HCl}$  at  $90^\circ\text{C}$  until completed sample dissolution. The resulting solutions were appropriately diluted for the analysis.

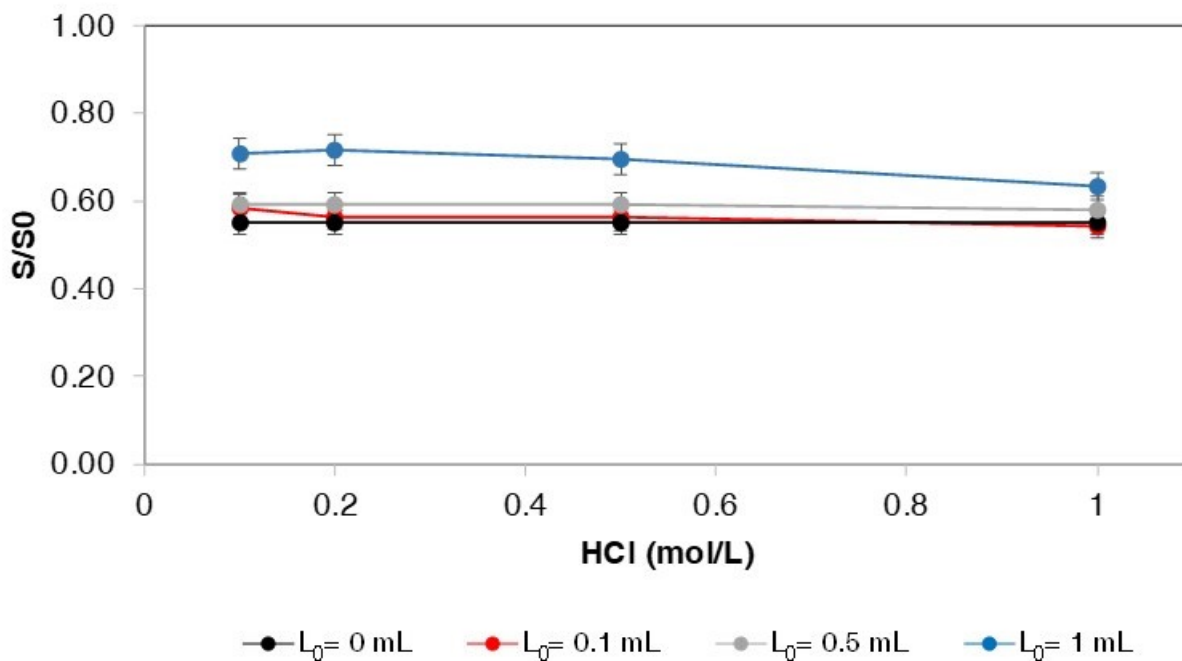
Before the analysis, a 5-points calibration curve ( $2\text{-}5\text{-}10\text{-}15\text{-}20 \mu\text{g L}^{-1}$ ) was built for both  $\text{Sb(III)}$  and  $\text{Bi(III)}$  in the no-hydrolysis chemifolds setup (Fig.S1A,  $1 \text{ mol L}^{-1}$   $\text{HCl}$ ) and in hydrolysis

configuration (Fig.S1B,  $L_0 = 0.5$  mL and  $0.5$  mol  $L^{-1}$  HCl for Bi,  $L_0 = 1$  mL and  $1$  mol  $L^{-1}$  HCl for Sb). Solutions arising from the mineralization of certified materials were properly diluted with water to match the calibration range.

### Additional results



**Figure S2.** FI-CVG-AFS experiments showing the evolution of  $50 \mu g L^{-1}$  Sb(III) (Fig.2A) and Bi(III) (Fig.2B) for the different hydrolysis coils with increasing HCl concentrations reported as log scale (0.02-0.05-0.1-0.5-1-2-5  $mol L^{-1}$ ), using the mixing sequences reported in Figure S1B. Reference signal  $S_0$  obtained under standard analytical conditions with the configuration reported in Figure S1A,  $1 mol L^{-1}$  HCl and 1% THB. Confidence interval was calculated at 95% from the mean of 3 replicates.



**Figure S3.** FI-CVG-AFS experiments for  $50 \mu\text{g L}^{-1}$  Sb in presence of  $75\text{-}15\text{-}15 \text{ mg L}^{-1}$  of Cr/V/Mo using the mixing sequences reported in Figure S1B. Reference signal  $S_0$  obtained with the configuration reported in Figure S1A,  $1 \text{ mol L}^{-1}$  HCl and 1% THB. Confidence interval was calculated at 95% from the mean of 3 replicates.

## References

1. A. D'Ulivo, I. Paolicchi, M. Onor, R. Zamboni and L. Lampugnani, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2009, **64**, 48-55.
2. E. Pitzalis, D. Angelini, M. C. Mascherpa and A. D'Ulivo, *Journal of Analytical Atomic Spectrometry*, 2018, **33**, 2160-2171.