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Combined effect of borohydride hydrolysis and chemical additives on lead determination by CVG in the presence of transition metals

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The aim of this investigation was to increase the tolerance limit of plumbane generation towards several transition metals by exploiting the hydrolysis products of borohydride – the hydridoboron intermediates (BH) – as a derivatization reagent instead of borohydride, alone or together with chemical masking agents (oxalic acid and thiourea). The BH intermediates were produced online at 0.1 mol L^{-1} HCl sample acidity in the presence of $K_3[Fe(CN)_6]$ (0.1 or 1% m/v) and by varying the hydrolysis coil volume (0–2000 μL) before mixing with the analyte. The simple use of BH intermediates alone obtained with 1500–2000 μL hydrolysis coil volume allowed the achievement of tolerance limits of 100 mg L^{-1} for Ni(II), Co(II), and Fe(III) and 105 mg L^{-1} for a mixture of Cr(III)/V(IV)/Mo(VI) (75 + 15 + 15 mg L^{-1}). The tolerance to the strong interfering action of Cu(II) was considerably improved but limited to 2 mg L^{-1}. To mitigate the interference caused by 1000 mg L^{-1} Fe(III), BH intermediates were used in combination with thiourea and oxalic acid. However, this approach did not enhance the tolerance to Cu(II) (2 mg L^{-1}), even in the presence of the masking agents. The established conditions allowed for the accurate determination of Pb in the complex matrix of SRM 663 (Cr–V steel) after sample dissolution with inorganic acids at high temperature.

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1. Introduction

Chemical vapor generation (CVG) using aqueous tetrahydridoborate (THB) derivatization coupled with atomic and mass spectrometry is a consolidated technique for trace element determination.[1,2] Mercury and the elements of group 14 (Ge, Sn and Pb), 15 (As, Sb, and Bi) and 16 (Se and Te) are the most frequently determined elements since the introduction of this technique in the early 1970s,[3,4] forming Hg^0 and volatile, stable, or fairly stable hydrides EH_n (E = Ge, Sn, Pb, $n = 4$; E = As, Sb, Bi, $n = 3$; E = Se, Te, $n = 2$). Over the years, the scope of CVG by THB derivatization has been expanded to many transition and noble metals,[2,5] even though the identity of their volatile derivatives remains mostly unknown. At present, the CVG technique has reached a good degree of rationalization, since most of the mechanisms involved in the formation of final hydrides – such as THB hydrolysis and hydrogen transfer from the reaction media to the analytical substrate – have been elucidated.[6–10] Interferences arising from transition and noble metals[1,2,11] and from the hydride-forming elements themselves[11–14] have long plagued CVG, and their mechanism of action is quite complex and not yet fully understood.[2,15] For analytical applications, interference control in CVG is typically achieved through the use of suitable chemical additives. Among them, L-cysteine and thiourea are the most popular and effective for many hydride forming elements such as Ge,[16] Sn[17,18] As,[18–20] Sb,[17,18,21] Bi[18] and Se,[22,23] either alone or in combination with other additives. A comprehensive survey of masking agents and additives used in CVG is provided in the monograph of Dědina and Tsalev.[1]

Within the family of hydride-forming elements, lead represents a singular case, as CVG of plumbane cannot be achieved without suitable additives – the most popular and effective being potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$ (FeC), which ensures generation yields >95%.[24] CVG of plumbane is affected by severe interferences, particularly those arising from transition metals. These are difficult to control because most masking agents which are effective for other hydride-forming elements fail or are much less effective in plumbane generation.[25] This may be due to the more complex formation mechanism of plumbane which, as recently demonstrated, involves the formation of intermediate non-volatile hydrides.[26] Atomization interferences in CVG of plumbane are not a problem in diffusion flame atomizers, such as the one used in the present study, as recently reported by Vlčková *et al.*[27]

Recent papers have reported detailed studies on the control of interferences in CVG of plumbane in acidic FeC reaction media. Deng *et al.*,[28] using CVG-ICPOES and FeC in HCl media in the presence of hexacyanoferrate (II), $K_4[Fe(CN)_6]$, observed

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no signal depression for an interferent concentration of 0.4 mg L^{-1}, except for Cu, whose tolerance limit was below 0.4 mg L^{-1}. Beltrán *et al.*[29] using FI-CVG-AFS and FeC in HCl media, investigated the effect of KI, L-cysteine and 1,10-phenantroline on the interference caused by 0.1–1.0 mg L^{-1} of As, Cu, Cr and Fe. The best control was achieved by KI, which improved the tolerance limit up to 0.3, 0.6 and 0.3 mg L^{-1} for As, Cu and Cr, respectively. In the absence of masking agents, Fe did not interfere up to 1.0 mg L^{-1}. Schlotthauer *et al.*,[30] using CVG-AAS in nitric acid plus borate buffer media and FeC, developed a CVG method for lead determination in natural water samples. They investigated the interference of hydride/cold vapor forming elements (As, Cd, Hg, Sb, Sn and Se) in the range from 0.005 to 0.05 mg L^{-1}, of transition metals (Ag, Co, Cr, Cu, Mo and Ni) in the range from 0.1 to 1.0 mg L^{-1}, and of Ba, Al, Fe and Mn at 10 mg L^{-1}. The most critical elements were Cu, Ag, Sb and Sn, for which tolerance limits ($\pm 10\%$ S/S_0) were around 0.1, 0.005, 0.05 and 0.02 mg L^{-1}, respectively. Among the tested masking agents – KI, L-cysteine, ascorbic acid and KSCN – only KSCN was effective, improving tolerance limits, particularly for Cu, up to 2.0 mg L^{-1}. The methods developed by Beltran *et al.*[29] and Schlotthauer *et al.*[30] were applied to natural water samples. The interference effect caused by high Co concentration was reported by Zheng *et al.*[31] using CVG-AFS: Co(II) concentrations of 10 and 100 mg L^{-1} caused 10% and 100% signal depression, respectively. The use of a mixture of KSCN, oxalic acid and 1,10-phenantroline dramatically improved the tolerance up to 1.4 g L^{-1} Co. Chuachuad and Tyson,[32] using THB immobilized on an anion-exchange resin and CVG-AAS, investigated the interference of several elements in the 0–100 mg L^{-1} range. For the transition metals tested, the approximate tolerance limits (mg L^{-1}) were reported as follows: Cr(VI) 100; V(V) < 10; Cu(II) and Fe(III) 1; Co(II), Ni(II), Zn(II) and Mn(II) < 1; Ag(I) < 0.1.

Recently, we reported the possibility of controlling interferences in CVG of stibane and bismuthane using the hydrolysis products of THB – without the use of any masking agents – by means of a simple reactor that allows the online generation of hydridoboron intermediates (BH).[33] It therefore seemed worthwhile to verify whether the use of BH intermediates could also be useful in controlling interferences in the CVG of plumbane, thereby enabling its application to samples of complex composition.

2. Materials and methods

Sodium tetrahydridoborate, powder, ≥98.0% and ammonia borane, powder, ≥95% (Sigma Aldrich). Sodium hydroxide (NaOH), 30%, TraceSELECT (Fluka). Hydrochloric acid (HCl), 37%, ACS reagent (Sigma Aldrich). Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, ≥99.0%, ACS reagent (Sigma-Aldrich). Copper(II) chloride, nickel(II) chloride, iron(III) chloride, and cobalt(II) chloride (Carlo Erba). Stock solutions of vanadium(IV), chromium(III) and molybdenum(VII) at 1000 mg L^{-1} (Fluka).

Working solutions of THB were freshly prepared and stabilized with NaOH (0.1 mol L^{-1}, unless otherwise specified). The solutions were clear and colourless and did not require filtration. Working solutions of Pb(II) were prepared by serial dilution of the commercial stock solution (1000 μg mL^{-1} in 2% HNO_3, Fluka) with HCl (final concentration 5×10^{-3} mol L^{-1}). Stock solutions of transition metals at 1000 mg L^{-1} in water were prepared from the corresponding chlorides. For Cr, V and Mo mixed solutions in water were prepared at 7.5–1.5–1.5 and at 75–15–15 mg L^{-1}, respectively. Working solutions of $K_3[Fe(CN)_6]$ were prepared by dilution in 0.1 mol L^{-1} HCl of a stock solution at 10% (v/v) in water, stored at 4 °C in a dark bottle.

A Standard Reference Material (SRM) 663 (chromium–vanadium steel) supplied by the National Institute of Standards and Technology (NIST), was chosen as a material of certain compositional complexity. Three independent samples were heated on a hot plate at 70 °C for three hours in 2 mL of HCl 5 M; then 0.25 mL of 65% HNO_3 was added and the heating was continued until completed sample dissolution. The resulting solutions were appropriately diluted for the analysis. All serial dilutions of the solutions, including dissolved samples and Pb(II) solutions, were made by weighing rather than by volumetric dilution.

Ultra-pure water purified by using a Purelab Pro (USF, ρ = 18.2 MΩ cm^{-1}) system was used in all the experiments.

Flow injection CVG (FI-CVG) experiments were carried out using a HPLC pump (Dionex IP20) with water as the carrier and working at 4 mL min^{-1}, and a six-way injection valve (Rheodyne, RH7725I) fitted with a 200 μL sample coil for Pb introduction. Ismatec Tygon microtubing of appropriate diameters was used with peristaltic pumps (Cole-Parmer Masterflex; Ismatec Reglo) for propelling borohydride and ferricyanide, and for the removal of waste solutions from the gas–liquid separator (GLS). Unless otherwise specified, reagent flow rates were 4 mL min^{-1} for ferricyanide and 2 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 (50 μL volume), which was obtained by connecting the mixing block to the GLS inlet with the aid of PTFE fittings (Bola, Germany). Both coils L_1 and L_2 were kept low in volume in order to reduce the contact time of plumbane with the solution. 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 Fig. 1). This was accomplished using various combinations of T-junctions (3-way mixing block, Kel-F, 0.8 mm i.d. channels, Ismatec) and mixing/reaction coils (Teflon PFA, 0.5–0.8 mm i.d.) of various volumes (from 0.1 to 2 mL).

A laboratory assembled atomic fluorescence spectrometer (AFS) was employed for the experiments. The AFS apparatus was described elsewhere.[34] A miniature Ar–H_2 diffusion flame (130 mL min^{-1} Ar, 80 mL min^{-1} H_2) supported on an 8 mm quartz tube was used as an atomizer for AFS measurements. A commercially available radiation source (Pb electrodeless

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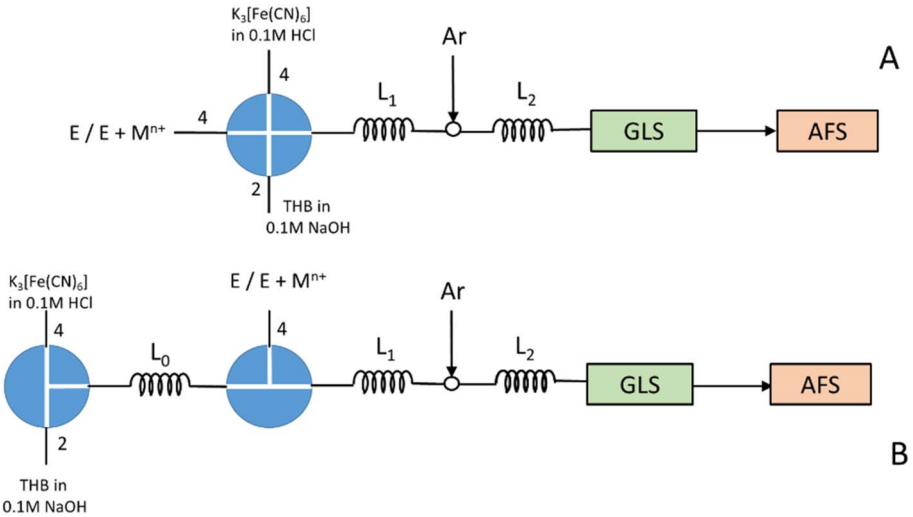

Fig. 1 Schematic representation of the chemifold setups used for the sequential addition of reagents. Numbers represent solution flow-rates in mL min^{-1}. The volume of reaction coil L_0 was set at 0 (setup A), or 0.1–0.5–1.0–1.5–2.0 mL (configuration B), L_1 and L_2 = 50 μL. Concentration of reagents: 1% $NaBH_4$ in 0.1 mol L^{-1} NaOH, 0.1 mol L^{-1} HCl. The Ar flow rate was set at 180 mL min^{-1}. Analyte (E) concentration was 100 ng mL^{-1}; transition metal concentration (M^{n+}) was varied between 1 and 1000 mg L^{-1}.

discharge lamp – EDL System 2 by PerkinElmer working at 400 mA and modulated at 500 Hz) was used.

3. Results and discussion

3.1. Plumbane generation using THB and its hydrolysis products (BH intermediates)

In light of our previous results with Sb and Bi,[33] the aim of this investigation was to determine whether BH intermediates can also help mitigate transition metal interferences in the CVG of lead. The evidence indicating that BH intermediates can efficiently generate plumbane (10–15% sensitivity loss compared to THB) was first reported in a recent paper investigating the mechanism of plumbane generation.[26] CVG of plumbane cannot be achieved in the absence of FeC (or any other suitable additive) and therefore it is not possible to evaluate the effect of BH intermediates alone as we previously did for Sb and Bi.[33] Furthermore, the generation efficiency of plumbane is strongly dependent on the acidity of the reaction medium, and for this reason the hydrolysis of THB was limited to the species produced using 0.1 mol L^{-1} HCl sample acidity. Acidities beyond this value are not suitable for the efficient generation of plumbane. Fig. 2 shows the dependence of the analytical signal as a function of hydrolysis coil volume. Specifically, the S/S_0 ratio is reported, where S corresponds to the signal obtained using the BH intermediates generated by THB in the hydrolysis loop L_0 (Fig. 1, configuration B, L_0 = 0.1–2.0 mL) and S_0 is the reference signal obtained using the analytical setup (Fig. 1, configuration A, L_0 = 0 mL) under standard analytical conditions (0.1 M HCl, 1.0% FeC). The relative sensitivity, S/S_0, represents a measure of the relative variation of the generation yield of plumbane, allowing the comparison of results obtained under different experimental conditions. We found that the relative sensitivity is barely dependent on the L_0 volume, and therefore on the time of hydrolysis of THB, as well as on FeC concentration (0.1% and 1%). It can be concluded that plumbane can be efficiently generated not only by the action of $[BH_4]^-$ ions but also by any BH intermediates obtained in a wide range of hydrolysis times , up to 2.5 s for L_0 = 1.5 mL.[26]

3.2. Effect of the volume of hydrolysis coil and $K_3[Fe(CN)_6]$ concentration on interferences

Fig. 3 summarizes the results obtained with the various interfering species at different hydrolysis coil volumes and at two different concentrations of FeC. Ferricyanide at 0.1% is the condition previously employed in mechanistic studies,[26]

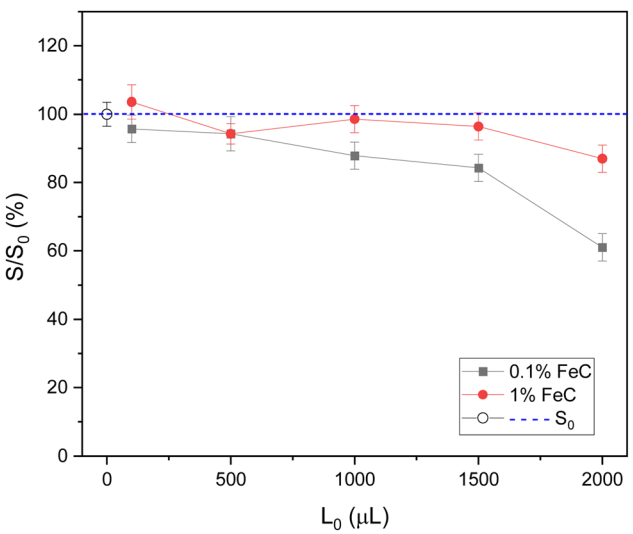

Fig. 2 FI-CVG-AFS experiments for 100 μg L^{-1} Pb using 0.1% or 1% FeC and the mixing sequences A (L_0 = 0 μL) and B (L_0 = 100–2000 μL) reported in Fig. 1. Reference signal S_0 obtained with the configuration having L_0 = 0. The confidence interval was calculated at 95% from the mean of 3 replicates.

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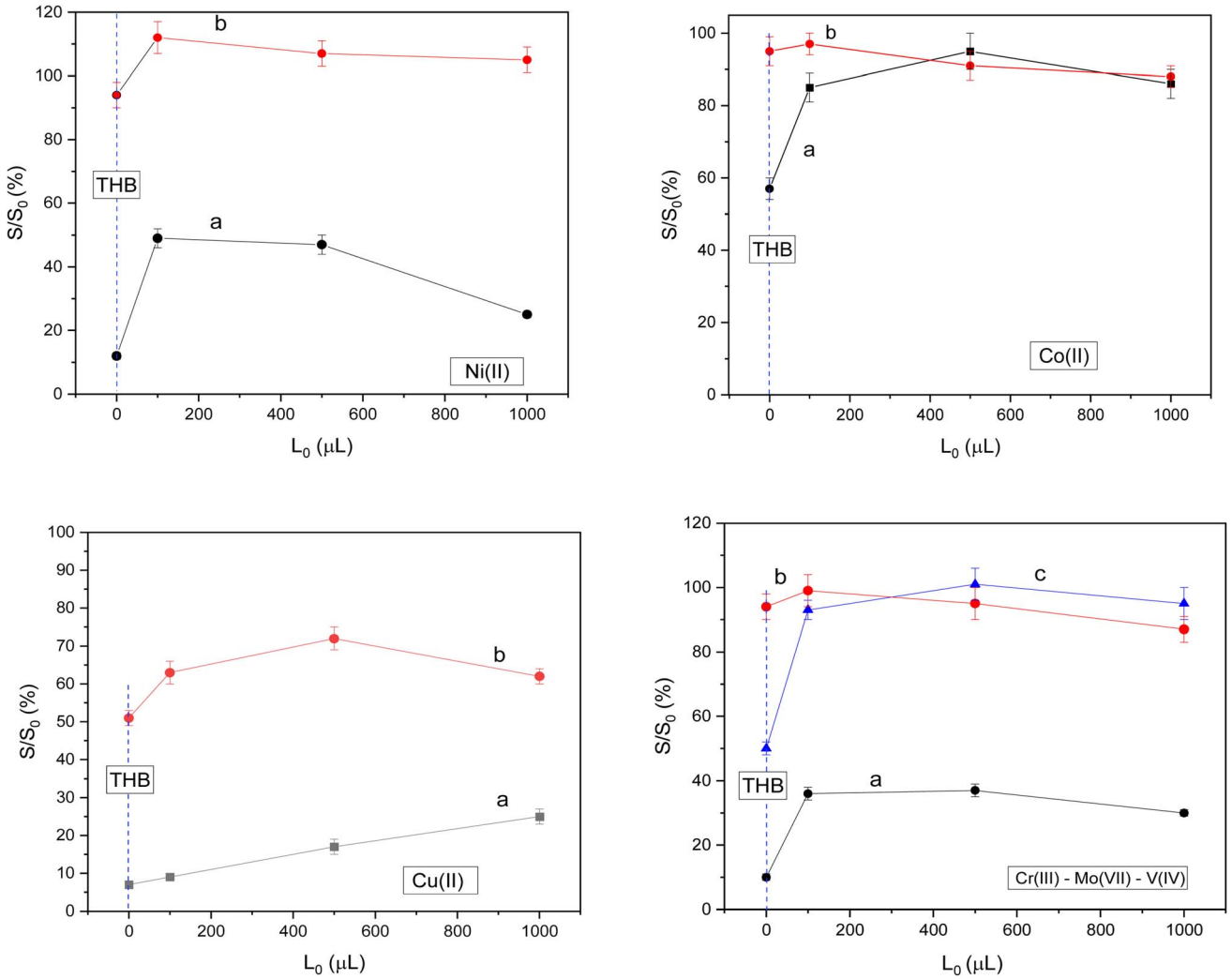

Fig. 3 Relative AFS signal for 100 μg L^{-1} Pb as a function of the hydrolysis coil volume (L_0). Curves a and b show measurements in the presence of interfering metals at two FeC concentrations: 0.1% (curve a) and 1.0% (curve b). The interfering metals were present at 100 mg L^{-1} Co and Ni, 1.0 mg L^{-1} Cu, and 105 mg L^{-1} total Cr (75) + Mo (15) + V (15). Curve c corresponds to 0.1% FeC with 10.5 mg L^{-1} total concentrations of Cr (7.5), Mo (1.5), and V (1.5). All measurements were obtained with setup B (Fig. 1), except those at $L_0 = 0$ mL, which were obtained with setup A (Fig. 1). Confidence intervals were calculated at 95% with $n = 3$.

whereas 1.0% FeC is more representative of analytical conditions.

The ability of BH intermediates to alleviate interferences is evident at 0.1% FeC (curve a and c). A hydrolysis coil of 0.1 mL appears indeed sufficient to overcome the interferences from 100 mg L^{-1} Co and 7.5–1.5–1.5 mg L^{-1} Cr/V/Mo. Nevertheless, these conditions are not able to properly control the interference of 100 mg L^{-1} Ni ($S/S_0 = 48\%$), 75–15–15 mg L^{-1} Cr/V/Mo ($S/S_0 = 10\%$, see curve a in Fig. 3), and 1 mg L^{-1} Cu ($S/S_0 = 7\%$). Increasing the volume of the hydrolysis coil up to 1 mL resulted in some improvement of S/S_0 only for Cu (from 7% at $L_0 = 0$ to 25% at $L_0 = 1$ mL). Thus, with the exception of 100 mg L^{-1} Co and 7.5–1.5–1.5 mg L^{-1} Cr/V/Mo, increasing the hydrolysis coil volume does not appear to reduce interference to a level suitable for analytical purposes. These conditions were achieved increasing the concentration of FeC to 1%. (Fig. 3, curve b for Co, Ni, and 75–15–15 mg L^{-1} Cr–Mo–V), with the only exception of Cu where signal depression still persists (Fig. 3, curve b), despite its concentration being two orders of magnitude lower than that of the other metals.

Using 0.1% FeC, and THB ($L_0 = 0$ mL) the interference of 10 mg L^{-1} Fe(III) is moderate ($S/S_0 = 80$) but it is severe at 100 mg L^{-1} ($S/S_0 = 3\%$) (data not shown for brevity). The use of BH intermediates is able to completely remove Fe(III) interference at 10 mg L^{-1} (Fig. 4, curve a) but not that at 100 mg L^{-1} Fe(III), regardless of hydrolysis coil length. Interestingly, increasing FeC to 1% removed the interference of 100 mg L^{-1} Fe(III) using THB ($L_0 = 0$ mL) and produced relative signal enhancement ($120 \leq S/S_0 \leq 134\%$) using BH intermediates ($L_0 = 100$–1000 mL) (Fig. 4, curve b). Under the same conditions (1% FeC), 1000 mg L^{-1} Fe(III) produced severe depression of the signal using either THB or BH intermediates (Fig. 4, curve c).

From Fig. 3 and 4, the role played by BH intermediates in improving interference control is clear at low FeC

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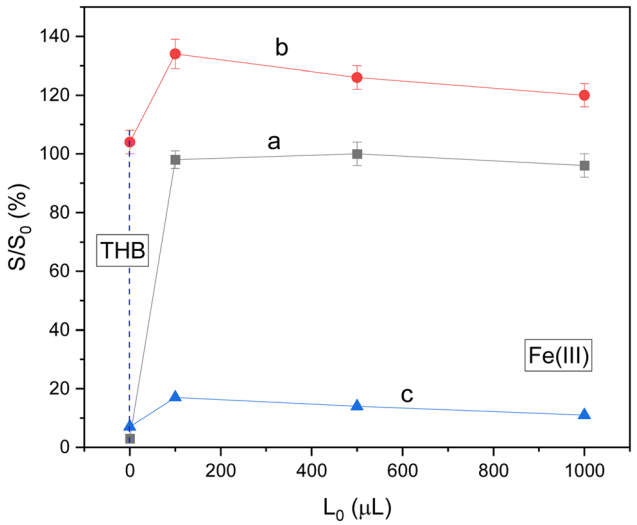

Fig. 4 Relative AFS signal for 100 μg L^{-1} Pb as a function of the volume of the hydrolysis coil, L_0, in the presence of Fe(III). (a) 100 mg L^{-1} Fe(III) – 0.1% FeC; (b) 100 mg L^{-1} Fe(III) – 1.0% FeC; (c) 1000 mg L^{-1} Fe(III) – 1.0% FeC. Measurements obtained with setup B (Fig. 1), except those at L_0 = 0 mL obtained with setup A (Fig. 1). Confidence intervals were calculated at 95% with n = 3.

concentrations. At high FeC concentrations, the role of the BH intermediates is much less pronounced because FeC starts behaving like a masking agent, playing a decisive role in eliminating or alleviating interferences.

Using 1% FeC and increasing the hydrolysis loop volume up to 2000 μL lead to better control of Cu interference, up to 2 mg L^{-1}, while maintaining good control of interference from other elements up to 100 mg L^{-1} (see Table 1).

These conditions (*i.e.*, 1% FeC and L_0 = 1500–2000 μL) ensure good interference control without using any additional reagents. Particularly, the tolerance toward Cu(II) interference is improved dramatically while the other interferences are not a problem using either THB (setup A, Fig. 1) or BH intermediates (setup B, Fig. 1) (Table 1, L_0 = 0). The surprisingly high tolerance of the system towards interferences which are observed in this work using THB under analytical conditions (Table 1, L_0 = 0) appears to be much better than that reported in the literature,[29–32] as already illustrated in the Introduction. Even though the comparison of performances obtained with different chemical conditions and reaction setups is a difficult task in CVG, we believe that in the present apparatus, the use of flow injection (200 μL sample volume) and the low volumes of the chemifold setup (L_0 = 0, and L_1 and L_2 = 50 μL) favored a fast separation of plumbane from the liquid phase, greatly improving interference control, as previously demonstrated by Ding and Sturgeon.[35]

Table 1 Interference effects using THB and BH intermediates[a]

	S/S_0[b] (%)							
	Ni(II)[c]	Co(II)[c]	Fe(III)[c]		Cr(III)–V(IV)–Mo(VI)[c]	Cu(II)[c]		
L_0 (μL)	100	100	100	1000	75–15–15	1.0	2.0	5.0
0	94	95	104	7	94	54	0	0
100	112	97	134	17	99	63	0	0
200	110	89	124	14	97	56	0	0
500	107	91	126	14	95	72	0	0
1000	105	88	120	11	87	62	0	0
1500	104	89	120	11	91	97	84	28
2000	103	84	87	11	97	97	94	40

[a] 1% FeC. [b] Max RSD ≤ 5%, n = 3. [c] Concentration in mg L^{-1}.

3.3. Masking agents

In an attempt achieve better control of the strong interference generated by Cu, as well as at higher Fe concentrations, the combined action of BH intermediates and masking agents was evaluated here for the first time. Ferricyanide concentration was tested at both 1% and 2% to investigate possible cooperative effects between this compound and the masking agents. For Cu interference, in the absence of any masking agents, no further significant improvements, compared to those reported in Fig. 3, were observed by increasing FeC to 2 and 3%.

Preliminary tests were performed on thiocyanate, thiourea, 1,10-phenantroline, and pyrocatechol (initial concentration set at 0.1 M), with 1% FeC. In the presence of 1 mg L^{-1} Cu, thiourea increased S/S_0 from 52% to 77% using THB (Fig. 1, setup A, L_0 = 0 mL), while 100% recovery was obtained with L_0 = 1 mL. Even with L_0 = 0.1 mL, S/S_0 increased from 69% to 92%. By contrast, thiocyanate seemed to further depress the Pb AFS signal, with S/S_0 equal to 42% (configuration A, L_0 = 0 μL) and 46% (configuration B, L_0 = 0.1 mL). 1,10-Phenantroline was less effective than thiourea at the same concentration (76% *vs.* 92%, 1 mg L^{-1} Cu and L_0 = 0.1 mL), and the same applies to pyrocatechol (72%, 1 mg L^{-1} Cu and L_0 = 0.1 mL).

Both thiocyanate and thiourea were ineffective in mitigating 1000 mg L^{-1} Fe(III) interference, regardless of their concentration (0.1 or 0.5 M). More efficient was the action of 0.1 M oxalic acid, if a comparison is made against the results reported in Table 1, for 1000 mg L^{-1} Fe(III), using both THB or BH intermediates. In the presence of oxalic acid S/S_0 increased from 7% up to 80% using THB (L_0 = 0 mL) and, using BH intermediates, from 17% up to 86% (L_0 = 0.1 mL), from 14 up to 97% (L_0 = 0.5 mL) and from 11 up to 90% (L_0 = 1 mL). We also verified that the addition of FeC in water after THB hydrolysis with HCl, in order to avoid FeC reduction from THB, was not helpful in managing copper interference.

The combined effect of 0.1 M oxalic acid and 0.1 M thiourea was then evaluated more systematically using 1% or 2% FeC and in the presence of 1000 mg L^{-1} Fe(III) or 1 mg L^{-1} Cu (Tables 2 and 3, respectively). It should be underlined that the masking agent must be added to the sample solution containing both Pb and the interferences, in the following order: first oxalic acid and then thiourea, to reduce and complex iron (the colour changes from dark yellow to light green).

From Table 2 it may be concluded that the presence of both masking agents is effective in controlling 1000 mg L^{-1} Fe(III) interference. Indeed, there is a wide choice of conditions allowing the removal of this interference; it can be controlled

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Table 2 Interference effects of 1000 mg L^{-1} Fe(III) on 100 μg L^{-1} Pb in the presence of thiourea and oxalic acid[a]

	S/S_0[b] (%)		
L_0 (μL)	1% FeC	TU–Ox–1% FeC	TU–Ox–2% FeC
0	7	112	88
500	14	106	120
1000	11	100	103
1500	11	91	100
2000	11	88	94

[a] Ox = 0.1 M oxalic acid, TU = 0.1 M thiourea. [b] Max RSD ≤ 5%, $n = 3$.

Table 3 Effect of BH intermediates and oxalic acid and thiourea on Cu(II) interference[a]

	S/S_0 (%)[b] [1 mg L^{-1} Cu(II)]		
L_0 (μL)	1% FeC	TU–Ox–1% FeC	TU–Ox–2% FeC
0	54	48	92
500	61	70	99
1000	62	82	91
1500	97	84	97
2000	97	85	92
	S/S_0[b]b (%) [2 mg L^{-1} Cu(II)]		
L_0 (μL)	1% FeC	TU–Ox–1% FeC	TU–Ox–2% FeC
0	0	15	41
500	0	28	60
1000	0	39	60
1500	84	49	63
2000	94	62	2
	S/S_0 (%)[b] [5 mg L^{-1} Cu(II)]		
L_0 (μL)	1% FeC	TU–Ox–1% FeC	TU–Ox–2% FeC
0	0	0	7
500	0	7	15
1000	0	9	16
1500	28	10	18
2000	4	12	18

[a] Ox = 0.1 M oxalic acid, TU = 0.1 M thiourea. [b] Max RSD ≤ 5%, $n = 3$.

using either THB or BH intermediates (with almost any hydrolysis coil volume) in the presence of thiourea + oxalic acid, and using either 1 or 2% FeC.

As shown by Table 3, the relative signal of Pb, with 1 mg L^{-1} Cu and both additives, was lower than that obtained with thiourea alone, but it approached almost 100% when working with 2% FeC and $L_0 = 0.5$ mL.

These conditions, while ensuring good control of both 1000 mg L^{-1} Fe(III) and 1.0 mg L^{-1} Cu(II) interferences (Tables 2 and 3), also maintained effective control of the interference from the other investigated metals: relative signals, S/S_0 (%), of 103, 107 and 113 were obtained in the presence of 100 mg L^{-1} Ni(II), 100 mg L^{-1} Co(II) and a mixture of Cr(III)–V(IV)–Mo(VI) (75 + 15 + 15 mg L^{-1}), respectively.

3.4. Applications

3.4.1. Water samples. Considering the good control of interferences achievable using setup B with a 2 mL hydrolysis loop (Table 1), these experimental conditions seem the simplest choice for Pb determination in water samples. The experimental setups A and B ($L_0 = 2$ mL) were tested on a seawater sample (CASS-4, Nearshore Seawater Reference Material for Trace Metals, NRC Canada). The lead concentration was below the detection limit of the present method. Nevertheless, some useful indications can be achieved by comparing the calibration graphs with both setups and built in water (A–H_2O and B–H_2O) or in the sample (A-CASS-4 and B-CASS4) (see Table 4).

The loss of sensitivity observed for setup B–H_2O with respect to setup A–H_2O is in agreement with the signal loss reported in Fig. 2, and it indicates that plumbane is produced less efficiently, either due to BH intermediates or their concentration. In contrast, the increase in sensitivity for setup B with CASS-4 compared to pure H_2O (about 20%) is a clear indication that plumbane formation is improved when the BH intermediates are formed in this type of matrix. This precludes the use of external calibration in pure water for lead determination in seawater. To overcome the limitations of standard addition, we propose better matching of the standard and sample matrices, for example by preparing standard solutions with higher chloride concentrations and by improving control of acidity.

3.4.2. Determination of Pb in SRM663 stainless steel. Due to the high content of Fe (94.4%) and considering the Cu concentration of 480 ± 10 μg g^{-1}, for determination of Pb (22 ± 1 μg g^{-1}) the analyses were performed using 2% FeC, 0.1 M thiourea and 0.1 M oxalic acid using setup B (Fig. 1) and $L_0 = 0.5$ mL. The selected protocol for the preparation consists of mild acid dissolution of approximately 0.1 g of sample with 2 mL of 5 mol L^{-1} HCl followed by 0.25 mL of 65% HNO_3. The dissolved samples were diluted with water in plastic 15 mL tubes, by weighing. Further dilutions were performed in order to obtain Fe and Cu concentrations of approximately 450 and 0.5 mg L^{-1} in the final solution, respectively, while Pb was around 10 μg L^{-1}. Since quantification by external calibration failed both with and without hydrolysis coil ($L_0 = 0$ mL and $L_0 = 0.1$–2 mL, hydrolysis mode), sample analysis by standard addition was pursued. The 0.5 mL hydrolysis loop was used for analysis with

Table 4 Comparison of calibration graphs[a]

Setup[b]	Sample	Slope (a.u.)	R^2	Slope ratio[c]
A	H_2O	14.06 ± 0.09	0.9993	1.00
A	CASS-4	13.53 ± 0.16	0.9973	0.96
B ($L_0 = 2$ mL)	H_2O	11.66 ± 0.01	0.9987	0.86
B ($L_0 = 2$ mL)	CASS-4	14.48 ± 0.07	0.9995	1.03

[a] Six lead concentrations in the range from 0 to 0.2 mg L^{-1}. [b] See Fig. 1. [c] Slope normalized to that of setup A–H_2O.

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setup B (Fig. 1). When working with BH intermediates (setup B, $L_0 = 500$ μL), the result was Pb = 20 ± 3 mg kg^{-1} ($N = 3$ and $\alpha = 0.05\%$), in accordance with the certified value (Pb = 22 ± 1 mg kg^{-1}). Using the same conditions (oxalic acid + thiourea, 2% FeC), the analysis without THB hydrolysis (setup A, $L_0 = 0$) resulted in a higher Pb concentration (Pb = 44 ± 15 mg kg^{-1}, $N = 3$ and $\alpha = 0.05\%$) compared to the certified value.

4. Conclusions

The ability of BH intermediates, generated by varying the time of hydrolysis of THB ($0 \leq L_0 \leq 2.0$ mL, 0.1 M HCl sample acidity), to produce plumbane is well evident using both 0.1% and 1.0% FeC. At the same time, BH intermediates present a better ability than THB in the control of interferences. The investigation could not be expanded to the study of different generation conditions because plumbane can be generated only in the presence of the additive and in a narrow range of sample acidity.

The best control of interferences is achieved by using 1.0% instead of 0.1% FeC. This effect can be attributed to the fact that FeC at higher concentrations, in addition to promoting plumbane formation, also starts to act as a masking agent itself. The use of a long hydrolysis time ($L_0 = 2.0$ mL) produces BH intermediates which are able to significantly improve the tolerance to Cu(II) interference up to 2.0 mg L^{-1}. Under the same conditions, good interference control of 100 mg L^{-1} of each Co(II), Ni(II), Fe(III) and Cr(III)–V(IV)–Mo(VI) (75 + 15 + 15 mg L^{-1}) is maintained compared to THB reduction ($L_0 = 0$ mL). Therefore, the use of BH intermediates ensures good interference control without the use of additional masking agents.

For the stainless steel sample the high iron content required the use of additional masking agents (oxalic acid + thiourea) and 2% FeC with BH intermediates ($L_0 = 0.5$ mL). The application to lead determination in stainless steel SRM663 gave results in good agreement with the certified value only using THB hydrolysis, while inaccurate results were obtained using THB ($L_0 = 0$ mL).

As final comments, it must be observed that BH intermediates seem to be less effective in interference control during plumbane generation compared to stibane and bismuthane generation.[33] This effect could be related to the complex mechanism of formation of plumbane,[26] which is probably more vulnerable to the presence of interfering species.

Author contributions

BC: methodology, data curation, writing – original draft. AD: conceptualization, supervision, methodology, formal analysis, writing – original draft. MO: investigation, methodology, validation, writing – review & editing. EP: methodology, writing – review & editing.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article are available on request.

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