



# Unveiling the mechanisms behind the chemical vapor generation of plumbane for trace analysis of lead

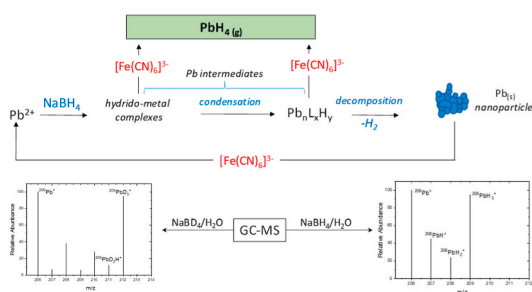
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## HIGHLIGHTS

- The mechanism of plumbane generated by  $\text{NaBH}_4$  derivatization have been clarified.
- Plumbane generated in analytical conditions has been identified by modified GC-MS.
- D-labelled experiments and GC-MS identified the mechanism of hydrogen transfer.
- The additive  $\text{K}_3\text{Fe}(\text{CN})_6$  reacts with Pb species formed in the early stage of reaction.
- Hydrolysis products of  $\text{NaBH}_4$  are active species in plumbane generation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The mechanisms controlling the generation of  $\text{PbH}_4$  by reaction of inorganic  $\text{Pb}(\text{II})$  with aqueous  $\text{NaBH}_4$  were investigated both in the presence and in the absence of the additive  $\text{K}_3\text{Fe}(\text{CN})_6$ . For the first time  $\text{PbH}_4$  has been identified in analytical chemical vapor generation (CVG) by using gas chromatographic mass spectrometry (GC-MS), which allows the use of deuterium labelled experiments. In the absence of the additive, under reaction conditions typically employed for trace lead determination by CVG,  $\text{Pb}(\text{II})$  is converted to solid species and no volatile lead species can be detected by either atomic or mass spectrometry for  $\text{Pb}(\text{II})$  concentration up to  $100 \text{ mg L}^{-1}$ . In alkaline conditions  $\text{Pb}(\text{II})$  substrates are unreactive towards  $\text{NaBH}_4$ . In the presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ , deuterium labelled experiments clearly indicated that the generated  $\text{PbH}_4$  is formed by the direct transfer of hydride from borane to lead atoms. Kinetic experiments were carried out to evaluate the rate of reduction of  $\text{K}_3\text{Fe}(\text{CN})_6$  by  $\text{NaBH}_4$ , the rate of hydrolysis of  $\text{NaBH}_4$  both in the presence and in the absence of  $\text{K}_3\text{Fe}(\text{CN})_6$ , and the rate of dihydrogen evolution following  $\text{NaBH}_4$  hydrolysis. The effect of delayed addition of  $\text{Pb}(\text{II})$  to  $\text{NaBH}_4\text{-HCl-Pb}(\text{II})$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ , and  $\text{K}_3\text{Fe}(\text{CN})_6$  to  $\text{NaBH}_4\text{-HCl-Pb}(\text{II})$  reaction mixtures on the efficiency of plumbane generation was investigated by continuous flow CVG coupled with atomic fluorescence spectrometry. The collected evidences, complemented with thermodynamic considerations and literature data, have made it possible to clarify long-standing controversial aspects related to the mechanism of plumbane generation and the role of  $\text{K}_3\text{Fe}(\text{CN})_6$  additive.

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## 1. Introduction

Chemical vapor generation (CVG) by aqueous boranes, mainly  $\text{NaBH}_4$  (THB), has been used for about fifty years for the determination and speciation of many elements for example: Ge, Sn, Pb, As, Sb, Bi, Se, Te, Zn, Cd, Hg, Cu and many other transition metals which can be converted to volatile hydrides, free atoms, and other species not yet identified [1–3]. Despite the popularity of CVG, the mechanisms governing this analytical derivatization reaction have been clarified only recently following a series of dedicated studies which started in 2003 [4]. Mechanism of hydrolysis of THB and some amine boranes, mechanism of hydrogen transfer and the mechanism of action of some chemical additives have been the targets of those dedicated investigations, which have been summarized in reviews and monographs [3,5–9]. However, the identity of some volatile derivatives and the mechanism of action of some chemical additives are among the still open and controversial issues in CVG.

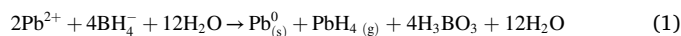
In the case of lead, the CVG of plumbane and any other volatile Pb species is not observed when trace Pb(II) reacts with aqueous THB (efficiency  $\ll 1\%$ ). In this case, the use of an additive is mandatory in order to achieve CVG of lead. Among the additives tested in aqueous phase CVG of lead, we can list  $\text{H}_2\text{O}_2$  [10–14],  $\text{Cr}_2\text{O}_7^{2-}$  + organic acids (lactic, malic and tartaric acid have been mostly employed) [15–17],  $\text{MnO}_4^-$  [11],  $\text{KBrO}_3$  [18],  $\text{Ce(IV)}$  [11],  $\text{Ce(III)}$  + oxalic acid [19],  $\text{S}_2\text{O}_8^{2-}$  [11,17],  $\text{K}_3\text{Mn(CN)}_6$  [20],  $\text{K}_3\text{Fe(CN)}_6$  [21–24],  $\text{K}_3\text{Fe(CN)}_6$  +  $\text{K}_4\text{Fe(CN)}_6$  [24], nitroso-R salts [25,26], PAN-S [1-(2-Pyridylazo)-2-naphthol-sulphonic acid] [26] (see Ref. [5] for a broader and more in-depth discussion on additives for CVG of plumbane). The volatile species, which is formed by reaction of Pb(II) with THB in the presence of some additives as  $\text{S}_2\text{O}_8^{2-}$  and  $\text{K}_3\text{Fe(CN)}_6$ , has been identified as plumbane,  $\text{PbH}_4$ , by Fourier transform infrared spectroscopy (FTIR) [27,28]. Gas chromatography mass spectrometry (GC-MS) has proven to be a powerful investigation tool in CVG of volatile hydrides when combined with deuterium labelled reagents [29–32]. However, some hydrides, as plumbane and hydrogen telluride, are completely retained by the GC apparatus, and GC-MS could not be employed for their detection in CVG.

The role played by additives in CVG of plumbane is unknown or controversial. As discussed in a recent review [5], for strong oxidizing agents it has been proposed that they are able to oxidize Pb(II) to Pb(IV), which is considered a more suitable substrate than Pb(II) for the formation of  $\text{PbH}_4$ . However, this hypothesis fails for non-oxidizing additives or for those additives that are weak oxidizing agents as hexacyanoferrate(III),  $[\text{Fe(CN)}_6]^{3-}$  (HCF). The additive HCF is largely employed because of its effectiveness at low concentration levels (3–30 mM), allowing to get almost quantitative efficiency of plumbane with moderate concentration of THB (250–300 mM) [33].

The mechanism of action of HCF, although it has been the subject of two dedicated investigations [23,24], is still debated [34,35]. The possible role played by the interaction of HCF ion with  $\text{BH}_4^-$  was investigated by D'Ulivo et al. through dedicated kinetics experiments in which HCF and  $\text{BH}_4^-$  were allowed to react for a controlled time before reaction with Pb(II) [23]. It was found that plumbane generation was achieved also in conditions under which the quantitative reduction of the additive HCF is expected according to kinetic calculations [23]. The fraction of HCF remaining unreacted was calculated according to the kinetic law proposed by Freund [36]. This led to conclude that plumbane generation was promoted by intermediate hydroboron species formed by the reaction of HCF with  $\text{BH}_4^-$  [23]. This hypothesis was criticized by Deng et al. because the intermediate hydridoboron species were not identified and, on the basis of their experiments, they suggested a different mechanism [24], which is discussed below. Actually the weak point of the mechanism based on the formation of HCF-THB intermediates [23] could be the kinetics of reduction of HCF with THB proposed by Freund [36], which has been criticized by Mochalov and Khain [37]. These authors reported that the effective species reducing HCF is the hydrolysis product  $\text{BH}_3\text{OH}^-$ , whereas both  $\text{BH}_4^-$  and

$\text{BH}_2(\text{OH})_2^-$  are unreactive with HCF [37]. These conclusions appear quite convincing because they were based on kinetic experiments using the sodium salts of the hydrolysis products of  $\text{BH}_4^-$ , i.e.  $\text{BH}_3\text{OH}^-$  and  $\text{BH}_2(\text{OH})_2^-$  [37]. This poses some doubts on the conclusion that plumbane generation can be promoted by an intermediate hydridoboron species formed by the reaction of HCF and  $\text{BH}_4^-$  [23].

In their study, Deng et al. [24] on the basis of CVG-ICP-OES experiments, which were complemented by X-ray diffraction spectrometry, proposed a reaction mechanism where the role of HCF is the reoxidation of the elemental lead that is produced by the dismutation reaction (1):



According to the authors, this reaction describes the fate of Pb(II) in the reaction with THB in the absence of the additive [24]. The mechanism based on reaction 1 was criticized [35] because in absence of HCF it predicts a yield of plumbane of 50%. This is in sharp contrast with the consolidated experimental evidence, confirmed also by Deng et al. [24] themselves, that at trace Pb(II) levels and in the absence of additives, less than 1% of lead is converted into volatile species [34,35].

In the light of the evidence reported in the literature it must be concluded that the mechanism of action of HCF in CVG of plumbane is still unknown, and it seems also clear that the fate of Pb(II) following its reaction with THB in the absence of any additives is not well known. The evidence, reported by Deng et al. [24] that the final product of the reaction  $\text{Pb(II)} + \text{THB}$  is elemental lead is not illustrative of the products which are formed in the early stage of reaction under analytical conditions (section 3.2.1). In order to understand the role of HCF in CVG of plumbane it is therefore important to first clarify what happens when Pb(II) reacts with THB in the absence of any additives.

The present work is divided into two parts, the first of which is dedicated to the comprehension of the mechanisms operating in the reaction of Pb(II) with THB under analytical conditions and in the absence of any additives. The second part investigated the role played by HCF in the modification of the reaction  $\text{Pb(II)} + \text{THB}$  leading to the formation of plumbane in CVG. The collected evidences, integrated with thermodynamic considerations and literature information have made it possible to clarify several aspects of a mechanism that have been controversial for a long time.

## 2. Experimental

### 2.1. Reagents

Sodium tetrahydridoborate, powder,  $\geq 98.0\%$  (Sigma Aldrich). Sodium hydroxide, Trace-Cert (Fluka). Hydrochloric acid, 37%, ACS (Sigma Aldrich).  $\text{TiO}_2$  powder ( $< 25$  nm) (Sigma Aldrich). Potassium hexacyanoferrate(III),  $\text{K}_3\text{Fe(CN)}_6$  (Sigma Aldrich).

Deuterium labelled reagents.  $\text{NaBD}_4$  98% atom D,  $\text{NaOD}$  30% w/w in  $\text{D}_2\text{O}$ , 99% atom D,  $\text{DCl}$  35% w/w in  $\text{D}_2\text{O}$ ,  $\geq 99\%$  atom D,  $\text{D}_2\text{O}$  99.9% atom D, were obtained from Sigma Aldrich.

Solution of lead enriched isotope, 100  $\mu\text{g mL}^{-1}$   $^{207}\text{Pb}$  in 5%  $\text{HNO}_3$  and 100  $\mu\text{g mL}^{-1}$   $^{206}\text{Pb}$  in 5%  $\text{HNO}_3$ , were obtained from Inorganic Ventures.

Working solutions of metal ions, Pb(II), were prepared from serial dilution of stock solutions (1000  $\mu\text{g mL}^{-1}$ , Fluka). Working solutions of  $\text{NaBH}_4$  and  $\text{NaBD}_4$  were freshly prepared and stabilized with  $\text{NaOH}$  or  $\text{NaOD}$  (0.1 M, unless otherwise specified). For scattering experiments, the solutions were filtered on 0.45  $\mu\text{m}$  regenerated cellulose membrane.

### 2.2. Apparatus

Atomic absorption (AAS) measurements were performed on lead ( $\lambda = 283.3$  nm; 0.7 nm bandwidth) using an AA spectrophotometer (PerkinElmer 2380) equipped with an electrodeless discharge lamp (PerkinElmer Type II). An electrothermally heated quartz tube (13 cm long,

14 mm od, 8 mm id) was used as an atomizer.

A laboratory assembled atomic fluorescence spectrometer (AFS) was employed for some experiments on CVG of lead. The AFS apparatus was described elsewhere [23,38]. A miniature Ar-H<sub>2</sub> diffusion flame (120 mL min<sup>-1</sup> Ar, 90 mL min<sup>-1</sup> H<sub>2</sub>) supported on an 8 mm quartz tube was used as an atomizer for AFS measurements.

GC-MS measurements were performed by an Agilent 6850 gas chromatograph equipped with Agilent 5975C mass spectrometric detector. The columns tested were a 30 m × 0.25 mm i.d. capillary column (0.25 μm DB5-MS-UI) and a short silica deactivated column (2 m long, 0.1 mm i.d.). Conditions for 30 m long capillary column: Injector T = 25 °C with 8:1 split, column T = 25 °C, interface T = 120 °C, source (EI 70 eV) T = 100 °C, carrier gas He 1.0 mL min<sup>-1</sup>. The conditions for the short 2 m long column, which has been adopted in an attempt to minimize the loss of Pb volatile species, were: injector T = 25 °C with 8:1 split, column T = 25 °C, interface T = 120 °C, source (EI 70 eV) T = 100 °C, carrier gas He 1.5 mL min<sup>-1</sup>.

UV-Vis spectrophotometric measurements were performed by using a V-750 spectrophotometer (Jasco) and 10 mm quartz cuvette (Helma).

Scattering measurements were performed by using a JASCO 821-FP spectrofluorimeter equipped with a flow cell, which is continuously flushed with by water carrier supplied by a HPLC pump (Dionex IP20). A six-way injection valve (Rheodyne, RH7725I) fitted with a 100 μL sample loop served for sample introduction. Excitation and emission wavelengths were set to 410 and 420 nm, respectively. The apparatus was tested by using an aqueous solution of TiO<sub>2</sub> nanoparticles (Fig. S2).

Kinetics of hydrogen generation during hydrolysis of THB in HCl media, in the presence and in the absence of K<sub>3</sub>Fe(CN)<sub>6</sub>, were measured using a laboratory pressure cell described elsewhere [39].

### 2.3. Chemical vapor generation

A continuous flow CVG (CF-CVG) was assembled by using peristaltic pumps (PP) (Cole-Parmer Masterflex; Ismatec Reglo). 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 μL sample loop.

Ismatec Tygon microtubings of appropriate diameters were used with the PP 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 mL min<sup>-1</sup> for the sample or blank, and 2 mL min<sup>-1</sup> 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 100 μL 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.).

For both CF-CVG and FI-CVG, 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. This was accomplished using various combination of T-junctions (3-way mixing block, Kel-F, 0.8 mm i.d. channels, Ismatec) and an X-junction (4-way mixing block, Kel-F, 0.8 mm i.d. channels, Ismatec), and mixing/reaction coils (Teflon PFA, 0.5–0.8 mmi.d.) of various volumes (from 15 to 2280 μL).

Batch CVG for GC-MS was achieved in 3 mL pyrex vial equipped with a rubber-teflon septa (Agilent). Unless otherwise specified, 1 mL of acidified analyte solution was placed in the vial and 0.5 mL NaBH<sub>4</sub> or NaBD<sub>4</sub> solution were added. 0.5–1.0 mL of the a headspace was sampled with a 2.5 mL volume gas tight syringe (Hamilton) and injected into GC-MS.

### 2.4. Reduction rate of [Fe(CN)<sub>6</sub>]<sup>3-</sup> by BH<sub>4</sub><sup>-</sup>

Batch experiments were performed using 10 mL polypropylene

tubes. 1 mL of 1.0 g L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] in 0.1 M HCl solution was placed in the tube, then 0.5 mL of 10 g L<sup>-1</sup> NaBH<sub>4</sub> in 0.1 M NaOH solution was added under magnetic stirring. The reaction was stopped by addition of 1 mL of 0.1 M NaOH after reaction times of 2, 5 and 10 s. Soon after, 1 mL of H<sub>2</sub>O was added and the UV-VIS spectra of the solution was recorded. The residual concentration of [Fe(CN)<sub>6</sub>]<sup>3-</sup> was measured at 420 nm.

In order to measure the absorbance of K<sub>3</sub>[Fe(CN)<sub>6</sub>] at t = 0 in solutions of similar composition to those that have been used for the above kinetic tests, the following measurements have been performed. 0.5 mL of 10 g L<sup>-1</sup> NaBH<sub>4</sub> were added to 1 mL 0.1 M HCl and the reaction was quenched by the addition of 1 mL of 0.5 M NaOH after reaction times of 2, 5 and 10 s, respectively. Then 1 mL of 1.0 g L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] in H<sub>2</sub>O solution was added to quenched solutions just before the spectrophotometric measurements. The absorbance (0.87 ± 0.02) resulted reproducible and independent of reaction times.

## 3. Results and discussion

### 3.1. Deuterium labelled experiments

Previous attempts to identify volatile species generated by CVG of Pb by GC-MS were unsuccessful using either NaBH<sub>4</sub> or NaBD<sub>4</sub> reagents and 30 m GC capillary column. The replacement of GC column by a short line of deactivate silica allowed detection of plumbane generated in batch CVG experiments (Fig. 1). It is the first time that plumbane is identified in analytical CVG by MS, which represents a more powerful investigation tool than FTIR.

Fig. 1 shows the mass spectra of plumbane obtained by CVG in the presence of the additive HCF. The spectra of PbH<sub>4</sub> were obtained using fully hydrogenated reaction media (Fig. 1a and d) and those of PbD<sub>4</sub> were achieved in fully deuterated reaction media (Fig. 1b and e) and using either <sup>207</sup>Pb or <sup>206</sup>Pb enriched isotopes. In agreement with literature data, the molecular ion is not present in the mass spectra of plumbane, a characteristic common also to the hydrides of Ge and Sn [40,41]. The mass spectra of plumbane generated by NaBD<sub>4</sub> in H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup> reaction media (Fig. 1c and f) is almost identical to that of PbD<sub>4</sub> (Fig. 1b and e), except that a small amount of hydrogen is incorporated in the final hydride.

This evidence confirms that also plumbane is formed by direct transfer of hydrogen from boron to lead, as the other volatile hydrides [29,30]. It is worth to underline that the ratio of intensities for the ions MD<sub>2</sub>H<sup>+</sup>/MD<sub>2</sub><sup>+</sup> (M = Ge, Sn, Pb) is about 0.12–0.13 for lead, which is significantly lower than that observed for germanium (0.4 – 1.4) and tin (0.25 – 0.9) [29]. This would indicate that the H-D exchange in the generation of PbH<sub>4</sub> is lower than in the generation of GeH<sub>4</sub> and SnH<sub>4</sub>.

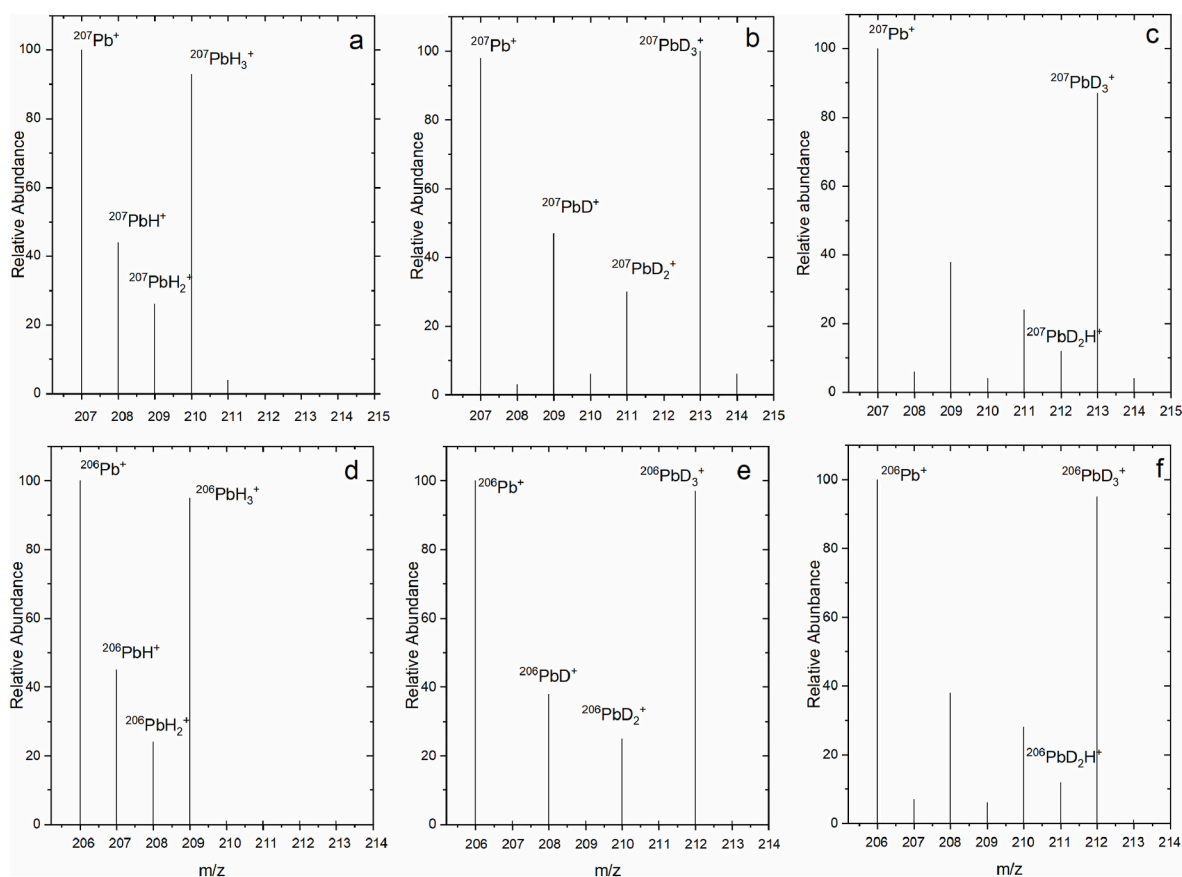
In the absence of HCF additive, no detectable lead containing species were detected by same modified GC-MS apparatus. As well, no signal was detected when the head space of the same experiment was injected into a AA spectrophotometer with quartz tube atomizer.

### 3.2. CVG of lead in the absence of any additives

#### 3.2.1. Qualitative experiments

As previously reported [23], during plumbane generation the pH of solution varied from about 1 up to 7 in less than a second and after 5 s the pH reached the final value of about 8.5. At the same time less than 48% (1s) and 63% (5s) of THB is hydrolyzed (section 3.3.2).

In this acidity range, for [Pb]<sub>tot</sub> below the micromolar level, the predominating Pb(II) substrates reacting with THB are the aqueous ions Pb<sup>2+</sup> and Pb(OH)<sup>+</sup> [42]. In absence of additives, Pb(II) substrates do not generate detectable volatile species and, in some cases, the formation of solid, non-volatile reaction products is observed, the identity of which is controversial [24,35]. Deng et al. [24] concluded that lead species are elemental lead on the basis of their experiments where a 10% THB solution added to an about 300 mM Pb(II), non-acidified solution, gave a



**Fig. 1.** Mass spectra of plumbane generated by reaction of  $^{207}\text{Pb}^{2+}$  (a–c) and  $^{206}\text{Pb}^{2+}$  ( $8 \mu\text{g Pb mL}^{-1}$ ) (d–f), in the presence of  $0.8 \text{ g L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$  and in different reaction media: 1 mL 0.1 M  $\text{HNO}_3$  (in  $\text{H}_2\text{O}$ ) + 0.5 mL 1%  $\text{NaBH}_4$  (in 0.1 M  $\text{NaOH}$ ) (a, d); 1 mL 0.1 M  $\text{DCl}$  (in  $\text{D}_2\text{O}$ ) + 0.5 mL 1.1%  $\text{NaBD}_4$  (in 0.1 M  $\text{NaOD/D}_2\text{O}$ ) (b, e); 1 mL 0.1 M  $\text{HCl}$  (in  $\text{H}_2\text{O}$ ) + 0.5 mL 1.1%  $\text{NaBD}_4$  (in 0.1 M  $\text{NaOH}$ ) (c, f).

black precipitate (yield 98%) which has been identified as elemental black lead by X-ray spectrometry. This conclusion has been criticized because the conditions are far from that of CVG, both in terms of pH and lead concentration [35]. In the case of Deng et al. [24] the reaction takes place in alkaline conditions and for lead concentration far exceeding the concentration threshold of 0.48 mM above which the speciation of lead changes dramatically compared with that observed at trace concentration. While at micromolar level of lead the predominant species are  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_3^-$ , for concentration far above 0.48 mM other species are predominant as  $\text{PbO}$  and polynuclear complexes as  $\text{Pb}_6(\text{OH})_8^{4+}$  and  $\text{Pb}_3(\text{OH})_4^{2+}$  [42].

Qualitative experiments, similar to those reported by Deng et al. [24], were carried out in conditions similar to those adopted in CVG, that is 1 mL of 1% THB solution in 0.1 M  $\text{NaOH}$  was added to 2 mL of aqueous, non-acidified  $\text{Pb}(\text{II})$  solutions. The formation of particulate matter was observed only for  $\text{Pb}(\text{II})$  concentration of  $1000 \text{ mg L}^{-1}$  (4.8 mM  $\text{Pb}$ ) but not for the more dilute solutions of 1.0, 10 and  $100 \text{ mg L}^{-1}$   $\text{Pb}(\text{II})$  (0.0048, 0.048 and 0.48 mM) as confirmed by scattering measurements. This is a clear indication that, in alkaline conditions, the reactivity of lead substrates toward THB is dependent on lead concentration and that the conclusion obtained at elevated lead concentration are not valid at trace  $\text{Pb}$  level. It can be concluded that, at trace  $\text{Pb}$  level and at  $\text{pH} > 12$  the predominating species is  $\text{Pb}(\text{OH})_3^-$  [42,43], which appears to be unreactive towards  $\text{BH}_4^-$ . This conclusion is supported by UV spectrophotometry (Fig. S1) where it is not evident the interaction of  $\text{BH}_4^-$  with the lead substrate  $\text{Pb}(\text{OH})_3^-$  in alkaline conditions. Increasing  $\text{Pb}$  concentration the predominating species is  $\text{PbO}$  [42], which seems to be reactive towards  $\text{BH}_4^-$ .

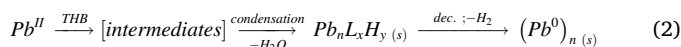
The same experiment reported above were performed under conditions closer to those of CVG, by using an acidified  $\text{Pb}(\text{II})$  solution [0.1 M

$\text{HCl}$ ;  $\text{Pb}(\text{II}) = 1.0, 10$  and  $100 \text{ mg L}^{-1}$ ] instead of neutral  $\text{Pb}(\text{II})$  solution. In this case, the formation of grey suspended particulate is observed soon after the addition of THB solution, independently of lead concentration. GC-MS and AAS measurements of the head space did not detect any volatile  $\text{Pb}$  species. The particulate formed upon addition of THB (at  $t = 0$ ), slowly redissolves and a residual scattering signal, equal to about 50% of the signal at  $t = 0$ , is observed after 60 min (Fig. S3).

The achieved evidence indicates that reactive species of  $\text{Pb}$  toward THB are present in analytical conditions. Before THB addition, at  $\text{pH}$  around 1 they could be  $\text{Pb}^{2+}$ , its chloride complexes and  $\text{Pb}(\text{OH})^+$  [42]. Upon THB addition the  $\text{pH}$  increases and, in this time interval, THB hydrolyzes and lead speciation changes. As demonstrated for other elements, as  $\text{Sb}$ ,  $\text{Bi}$ ,  $\text{Sn}$  [44] and  $\text{Cd}$  [45], the kinetics involved in the change of speciation of the analytical substrates is slower than  $\text{pH}$  equilibration. Therefore it is likely that, also in CVG of lead, reactive analytical substrates are still present in the early stage of reaction (reaction time  $\ll 1\text{s}$ ); they can react with  $\text{BH}_4^-$ , and other hydridoboron species that are formed in this reaction conditions.

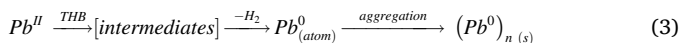
### 3.2.2. On the nature of lead reaction products

There are no doubts that the final fate of the reaction products arising from reaction of inorganic  $\text{Pb}(\text{II})$  with aqueous  $\text{NaBH}_4$  is their conversion to elemental lead under the form of lead nanoparticles (NP) [9,46]. This reaction can take place through different reaction pathways, most likely through the formation of non-volatile intermediate hydrides, herein termed as ‘intermediates’, and/or hydrido-metal complexes (reaction 2):

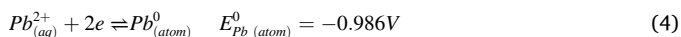


The existence of lead hydrides other than  $\text{PbH}_4$  is supported by evidence reported by Wang and Andrews [47], who identified also  $\text{PbH}_2$ ,  $\text{Pb}_2\text{H}_2$  and  $\text{Pb}_2\text{H}_4$  by laser-ablation matrix-isolation infrared spectroscopy. However, the intermediates can also have the characteristic of hydrido-metal complexes (HMCs), which can undergo condensation reactions [32] forming higher molecular weight polynuclear lead HMCs,  $\text{Pb}_n\text{L}_x\text{H}_y$  ( $L = \text{OH}, \text{Cl}$  etc). These compounds, HMCs and polynuclear lead HMCs, are thermally unstable and decompose by releasing dihydrogen to give lead nanoparticles,  $(\text{Pb}^0)_n$ , the final products [46].

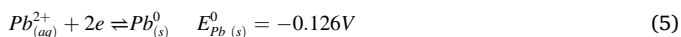
In another possible reaction pathway, the formation of the final lead products occurs through the aggregation of free Pb atoms (reaction 3):



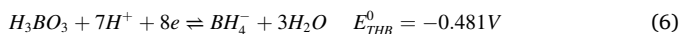
According to Mondal et al. [48], reaction 3 is less favorable than reaction 2 on the basis of the standard electrode potential for the reactions  $\text{M}_{(\text{aq})}^{n+} + ne \rightleftharpoons \text{M}_{(\text{s})}^0$  and  $\text{M}_{(\text{aq})}^{n+} + ne \rightleftharpoons \text{M}_{(\text{atom})}^0$ . The calculation, performed according to the method proposed by Mondal et al. [48] (section S2.1), gave the standard electrode potential for the formation of lead atoms,  $E_{\text{Pb}_{(\text{atom})}}^0$ :



Which is much more negative than the value of  $E_{\text{Pb}_{(\text{s})}}^0$  reported in literature [49]:



and of the standard electrode potential of tetrahydridoborate [49]:

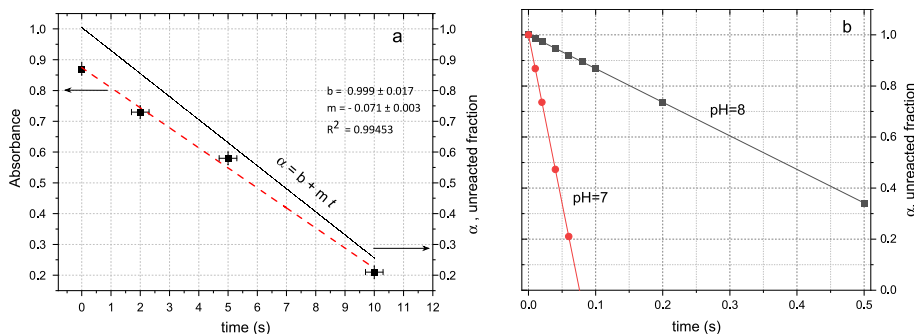


Considering the reaction conditions for CVG of plumbane, which are described at the beginning of section 3.2.1., it is possible to verify that for lead substrates as  $\text{Pb}^{2+}$  and  $\text{Pb}(\text{OH})^+$  their reduction to atomic state by THB, in the range of pH from 1 to 8, is not feasible from a thermodynamic point of view (see section S2.1 and Fig. S4).

### 3.3. CVG of lead in the presence of the additive hexacyanoferrate(III)

#### 3.3.1. The rate of reduction of hexacyanoferrate(III) by THB

According to the discussion reported in the introduction, the kinetics and mechanism of reduction of  $[\text{Fe}(\text{CN})_6]^{3-}$  by  $\text{BH}_4^-$  reported in the literature should be used with caution when applied to conditions typically occurring in CVG. It seemed therefore necessary to perform simple batch experiments in order to verify the rate of reduction of  $[\text{Fe}(\text{CN})_6]^{3-}$  by  $\text{BH}_4^-$  under CVG conditions. This has been simply performed by measuring the residual concentration of  $[\text{Fe}(\text{CN})_6]^{3-}$  by spectrophotometry, after its reaction with  $\text{BH}_4^-$  for reaction times in the range from 0 to 10 s (see section 2.4 for experimental details). The results, reported in Fig. 2a can be compared with the unreacted fraction,  $\alpha$ , expected by the kinetic law proposed by Freund [36] (Fig. 2b). It is clear that under the conditions employed in CVG of plumbane the rate of



**Fig. 2.** (a) Absorbance of a solution of  $[\text{Fe}(\text{CN})_6]^{3-}$  at 420 nm after reaction with  $\text{BH}_4^-$  for 0, 2, 5 and 10 s reaction time (red dashed line) (see section 2.4 for details). The estimated fraction of  $[\text{Fe}(\text{CN})_6]^{3-}$  left unreacted,  $\alpha$ , is given in the plot (black line) together with linear fitting equation; (b) percentage of  $[\text{Fe}(\text{CN})_6]^{3-}$  left unreacted after reduction with THB, as calculated according the kinetic law reported by Freund [36]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

disappearance of  $[\text{Fe}(\text{CN})_6]^{3-}$  is much lower than the predictions of Freund's law. This implies that plumbane is generated and stripped out when the concentration of  $[\text{Fe}(\text{CN})_6]^{3-}$  in solution is relatively high, likely more than 70% of its initial concentration considering that reaction times in CVG apparatus are below 3 s (Section S4 and Table S1). It follows that the enhancement in plumbane generation cannot be addressed exclusively to formation of intermediate hydridoboron species produced by reaction of  $[\text{Fe}(\text{CN})_6]^{3-}$  with  $\text{BH}_4^-$  or its hydrolysis products [23]. This is reasonable because the contribution of possible reactions of  $[\text{Fe}(\text{CN})_6]^{3-}$  with leads species, HMCs and elemental Pb, which are formed by reaction of Pb(II) with THB (reaction 2) cannot be ignored.

The evidence that  $\text{PbH}_4$  is generated and stripped out from a reaction environment where there is still a relatively high concentration of HCF, could be an indication that plumbane presents a limited reactivity with the additive. If plumbane is bubbled in a 2 mL aqueous solution at different pH and composition (section S3) it is interesting to observe as the presence of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  at different acidities (pH in the range from about 1 to 13) did not result in a significant signal depression compared to pure aqueous solution in the same pH range (Fig. S7). It is clear that in bubbling experiments the interaction of plumbane with the solution is less effective compared with that occurring in a CVG apparatus, but in this case the concentration of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in the trap (1% m/v) is at least 30 times higher than that occurring in the CVG apparatus after mixing all reagents.

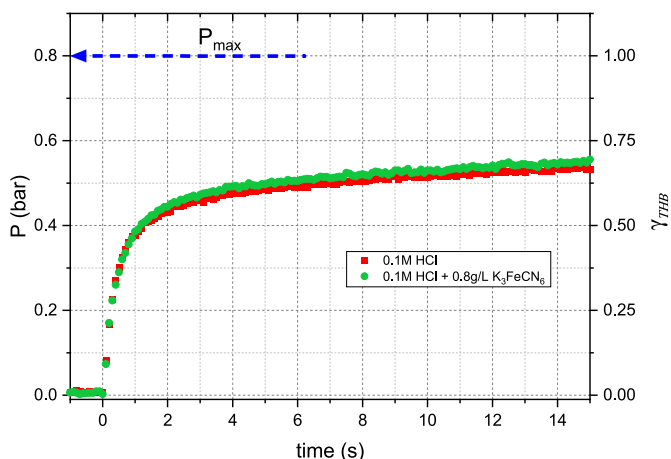
It can be argued that the additive HCF is almost unreactive with plumbane, while it is instead reactive with lead intermediates promoting thus the formation of plumbane.

#### 3.3.2. The rates of hydrolysis of THB and hydrogen evolution

The rate of hydrolysis of THB was tested by measuring the rate of hydrogen evolved during the hydrolysis reaction. The measurement was carried by monitoring the pressure of the head space of a batch reaction system. The results are reported in Fig. 3.

The same concentration of reagents and the relative volume ratios (1 volume of THB solution reacts with 2 vol of sample solution) of the continuous flow reaction system described in next section 3.3.3. have been used. As can be observed, the hydrolysis of THB (88 mM after mixing) appears to be hardly affected by the presence of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (1.6 mM after mixing).

Concerning the assumption that the same kinetics of hydrolysis occur in both batch and continuous flow reaction systems, it should be considered that the mixing times of batch and continuous flow reaction systems are about 500 [50] and 30 ms [44], respectively. For residence time  $\geq 500$  ms, it will be assumed that the kinetics of hydrogen evolution reported in Fig. 3 are valid also for the continuous flow reaction system. The data reported in Fig. 3 are important, among the others, for the evaluation of the correct residence times (section S4) in the continuous flow generation system (section 3.3.3).

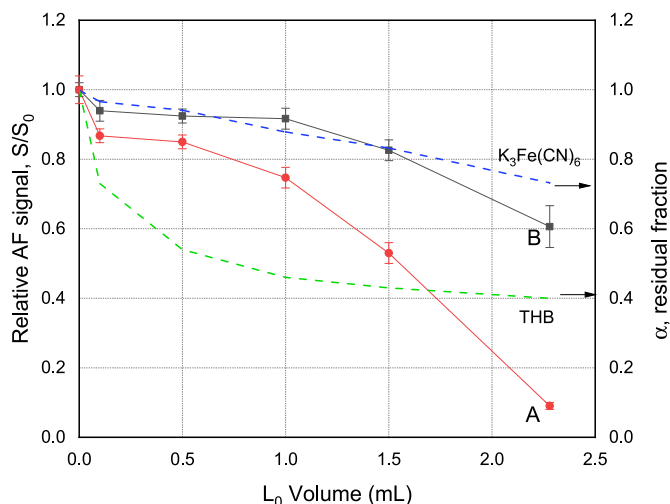


**Fig. 3.** Experiments on the kinetic of hydrogen evolution during hydrolysis of  $\text{NaBH}_4$ . Ordinate axes: left, pressure of hydrogen in the headspace of reaction cell; right,  $\gamma_{\text{THB}} = (P/P_{\text{max}})$ , fraction of hydrolyzed  $\text{NaBH}_4$ .  $P_{\text{max}}$  is the pressure after complete hydrolysis (30 min). Conditions: 0.5 mL of 1% w/v  $\text{NaBH}_4$  (in 0.1M  $\text{NaOH}$ ) added either to 1 mL of 0.1 M  $\text{HCl}$  or to 1 mL of 0.1 M  $\text{HCl}$ + 0.8 g  $\text{L}^{-1}$   $\text{K}_3\text{Fe}(\text{CN})_6$ . Acquisition rate  $10 \text{ s}^{-1}$ .

### 3.3.3. CVG of plumbane using sequential addition of reagents

Experiments involving the sequential addition of reagents have been made by CF-CVG-AFS using the chemifold setups reported in Fig. 4. The results are reported in Fig. 5.

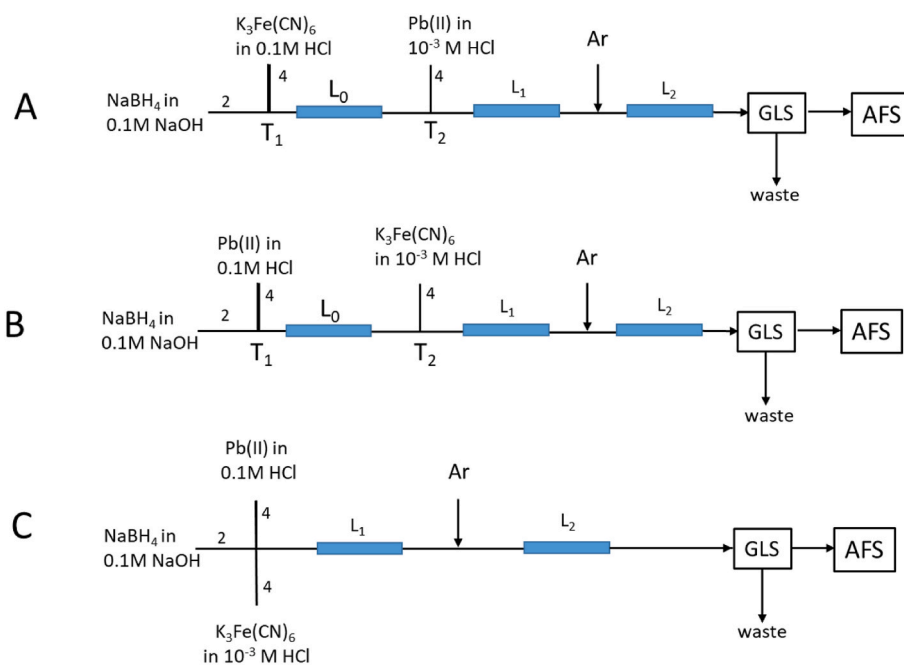
When  $\text{Pb}(\text{II})$  is added in  $T_2$  to a solution where THB is hydrolyzed in  $L_0$  for a controlled time in the presence of  $[\text{Fe}(\text{CN})_6]^{3-}$  (chemifold setup A, Fig. 4), the efficiency of plumbane generation (plot A, Fig. 5) is always lower compared to that observed when  $[\text{Fe}(\text{CN})_6]^{3-}$  is added in  $T_2$  to a solution in which THB is hydrolyzed in  $L_0$  in the presence of  $\text{Pb}(\text{II})$  (chemifold setup B, Fig. 4) (plot B, Fig. 5). This discrepancy could not be caused by the high fraction of THB which is lost in  $L_0$  during hydrolysis because for both setups A and B the fraction of hydrolyzed THB in  $L_0$  is almost the same according to the kinetics reported in Fig. 3. Not even the decrease of concentration of  $[\text{Fe}(\text{CN})_6]^{3-}$  can be at the origin of lower



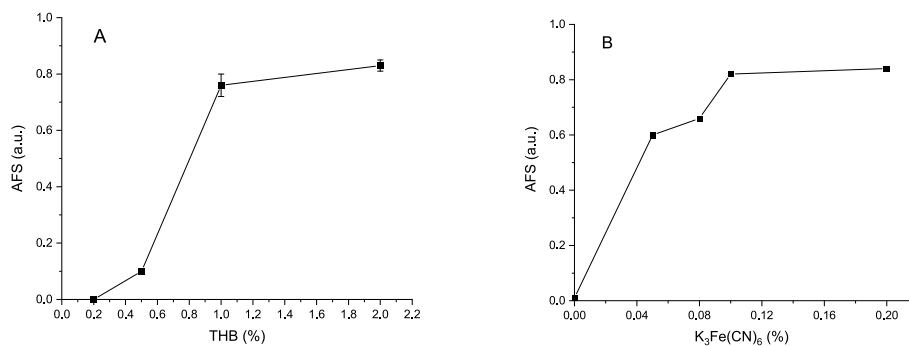
**Fig. 5.** Sensitivity observed in CVG of plumbane (left axis) using the chemifold setups A and B, reported in Fig. 4.  $S_0$  is the reference signal obtained with chemifolds setup C (Fig. 4). Dotted lines are the residual fraction of  $\text{K}_3\text{Fe}(\text{CN})_6$  and THB (right axis) after reaction in  $L_0$ . Corrected residence times in reaction loop  $L_0$  are employed for the estimation of residual fraction (section S4 and Table S1).

generation efficiency of plumbane for setup A. Indeed, less than 30%  $[\text{Fe}(\text{CN})_6]^{3-}$  is reduced in  $L_0$  (Fig. 5), which can cause only a moderate decrease of AF signal ( $<10\%$ ) as can be deduced from Fig. 6B.

The reason for which the delayed addition of  $\text{K}_3\text{Fe}(\text{CN})_6$  (plot B, Fig. 5) is more effective than the delayed addition of  $\text{Pb}(\text{II})$  (plot A, Fig. 5) to the reaction mixture must be searched in the nature of lead substrates which are present in  $T_2$ . In the first case (plot B), the reaction of THB with  $\text{Pb}(\text{II})$  in  $L_0$  forms lead intermediates that already contain  $\text{Pb-H}$  bonds (reaction 2). In the second case (plot A), the formation of lead intermediates starts in  $T_2$  but in a reaction environment in which the concentration of reductant is depleted. It appears important that the additive can interact with lead substrates in the early stage of reaction,



**Fig. 4.** 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 loop  $L_0$  varied from 100 to 2280  $\mu\text{L}$ ,  $L_1$  and  $L_2 = 100 \mu\text{L}$ . Concentration of reagents: 1%  $\text{NaBH}_4$ ; 100 ng  $\text{Pb}(\text{II}) \text{mL}^{-1}$ ; 0.8 g  $\text{L}^{-1}$   $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Ar flow-rate 100  $\text{mL min}^{-1}$ .



**Fig. 6.** Effects of THB (A) and  $K_3Fe(CN)_6$  concentration using CF-CVG-AFS and chemifolds setup C (see Fig. 4). Conditions:  $100 \text{ ng mL}^{-1}$  Pb(II) in 0.1 M HCl for (A) and (B);  $1.0 \text{ g L}^{-1}$   $K_3Fe(CN)_6$  (A); 1% THB in 0.1 M NaOH (B).

when suitable lead intermediates are present. The signal decrease with increasing residence time in  $L_0$  (plot B) can be attributed to the limited lifetime of lead intermediates which evolve to elemental lead. In this case, the elemental lead must be reoxidized to Pb(II) by the additive, and the plumbane formation takes place in conditions similar to those of plot A. The relative AF signal, for both plots A and B, decreases for  $L_0 \geq 1.0$  mL where the residual fraction of THB remains almost constant (Fig. 5). This confirms that the decrease of generation efficiency of plumbane is mainly due to the loss of suitable lead intermediates.

As a final observation, it is interesting to note that the relative signals obtained with reaction loop  $L_0$  from 0.5 to 1.5 mL are in the range from 0.9 to 0.5 for both setups A and B, and in the same conditions the residual fraction of reductant is lower than 0.5 (Fig. 5). Using the analytical setup C (Fig. 4) the relative AF signal drops to 0.1 when the concentration of  $NaBH_4$  is halved, i.e. from 1 to 0.5% (Fig. 6A). The concentration of reductant, after mixing of all reagents, is diluted by a factor 2/10 in setup C, and by a factor 2/6 in both setups A and B (Fig. 4), which can contribute to decrease the signal more than expected. However, it must be also considered that, according to stepwise mechanism of hydrolysis of THB [50]:



X = OH,  $H_2O$ , Cl; the charge  $z = 0, \pm 1$

a 50% hydrolysis of  $n$  moles of THB in  $L_0$  leads to the disappearance of  $n$  moles of each  $BH_4^-$  and  $[BH_3X]^z$ , and to the formation of  $n$  moles of  $[BH_2X_2]^z$ . These are not the same conditions that can be achieved halving to  $n/2$  the initial concentration of THB because the hydrolysis leads to formation of  $n/2$  mol of  $[BH_2X_2]^z$ . An important conclusion that follows from the above observations is that the hydridoboron intermediates  $[BH_2X_2]^z$  and  $[BHX_3]^z$  play a role in CVG of plumbane using chemifolds setup A (Fig. 4). Indeed, by combining the information of Figs. 3 and 5A, they are the only possible species in the reaction system for  $L_0 \geq 1.0$  mL.

### 3.4. The role of $[Fe(CN)_6]^{3-}$ in plumbane generation

Considering the evidence that a significant concentration of  $[Fe(CN)_6]^{3-}$  is always present in solution during CVG of plumbane (Figs. 5 and 2a), the role played by the additive must take into account its possible interaction with both the borane and the analyte as detailed below.

#### 3.4.1. Additive-borane complexes formation

The evidence reported in Fig. 5, cannot exclude that the additive can form complexes with borane/hydridoboron species, which are able to promote the formation of plumbane from Pb(II) substrates, as proposed previously [23]. Nevertheless, some evidences reported in previous sections are not in favor of the interaction of  $[Fe(CN)_6]^{3-}$  with THB.

First, the results of deuterium labelled experiments. The generation of  $PbD_4$  by  $BD_4^-$  in  $H_2O/H^+$  media takes place by direct transfer of deuterium from borane to lead with a small amount fraction of hydrogen incorporated in the final hydride (section 3.1.). It seems unlikely that  $[Fe(CN)_6]^{3-}$  could be involved in the formation of active hydridoboron intermediates without any perturbation of the mechanism of transfer of hydrogen taking place [23]. Second, the rate of reduction of  $[Fe(CN)_6]^{3-}$  is relatively slow (section 3.3.1). In an analytical reactor system ( $L_1 = 100 \mu\text{L}$ , Fig. 4C) reaction times are around 0.3 s (Table S1) and about 98% of  $[Fe(CN)_6]^{3-}$  is left unreacted and only the remaining 2% could be involved in complex formation with THB. This means that a maximum concentration of 0.02 mM HCF-borane complex is available in reaction loop  $L_1$ , which seems quite low to perform the fast and efficient conversion of Pb(II) to  $PbH_4$  in a wide range of Pb concentration.

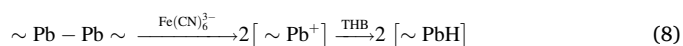
In the light of above considerations, the role played by HCF-borane complexes in CVG of plumbane appears to be unlikely or of little relevance.

#### 3.4.2. Additive reaction with analytical substrates

The moderate oxidizing power of  $[Fe(CN)_6]^{3-}$  ( $E^0 = 0.36 \text{ V}$ ) eliminates the possibility that it can act by oxidizing Pb(II) to Pb(IV) ( $E^0 = 1.46 \text{ V}$ ), while it can oxidize elemental lead to  $Pb^{2+}$  ( $E^0 = -0.126 \text{ V}$ ) and  $Pb(OH)^+$  ( $E^0 = 0.102 \text{ V}$ ). A reaction pathway that is based on the reoxidation of elemental lead to Pb(II) as proposed by Deng et al. [24], is devoid of meaning because in any case inorganic Pb(II) is not a good precursor for  $PbH_4$ .

The CVG of  $PbH_4$ , from both  $Pb^{2+}$  and  $PbOH^+$  substrates, does not appear to be hindered by thermodynamic factors, as it can be concluded on the base of standard electrode potentials (Section S2.2.). The reaction passes through the formation of lead intermediates which do not evolve to volatile plumbane. Therefore, a more reasonable hypothesis is that  $[Fe(CN)_6]^{3-}$  interacts with lead intermediates in an early stage of reaction 2, driving their conversion to plumbane before they can decompose to element, as supported by the evidence reported in Fig. 5 (plot B).

The nature of the intermediates should be that of non-volatile compounds containing Pb–H, Pb–Pb and Pb–H–Pb bonds [47]. It is interesting to note that from the energetic point of view, for lead hydrides and lead alkyls, the IV state is preferred over the II state, contrary to inorganic lead compounds where the II state is preferred [47,51]. One of the reaction performed by additive could be therefore that of selectively oxidize the Pb–Pb bonds, to form cationic species that are converted to hydride by THB:



For example, in a simple case,  $H_3Pb-PbH_3 \rightarrow 2 PbH_3^+ \rightarrow PbH_4$

However, as discussed in section 3.2.2., it is reasonable that more complex, nonvolatile polynuclear lead HMCs,  $Pb_nL_xH_y(s)$  ( $L = OH, Cl$  etc) are formed. In this case  $[Fe(CN)_6]^{3-}$  can convert the

polynuclear lead HMCs to mononuclear fragments, which are converted to hydrides as in reaction 8. Considering the preferred IV state over the II state for lead hydrides [51], it could be also possible that hexacyanoferrate(III) is able to promote formation of Pb(IV) hydrides from Pb(II) hydrides, while it cannot promote the conversion of inorganic Pb(II) to Pb(IV) species.

#### 3.4.3. Additive reaction with lead hydrides

From a thermodynamic point of view, it is reasonable to expect that a hydride can react with an oxidizing species. The fact that this does not always happen can be attributed to the kinetics of the reactions involved in the CVG process. An example is reported in section 3.3.1, where the reaction between THB and  $[\text{Fe}(\text{CN})_6]^{3-}$  is characterized by relatively slow kinetics, which allows for almost constant concentrations of additive during the generation of  $\text{PbH}_4$ . By bubbling  $\text{PbH}_4$  into a  $[\text{Fe}(\text{CN})_6]^{3-}$  solution at different pHs, no significant interaction between hydride and oxidant is noticed (section 3.3.1 and section S3). This indicates that  $[\text{Fe}(\text{CN})_6]^{3-}$  slowly oxidizes the Pb–H bonds in the  $\text{PbH}_4$ . This characteristic is probably maintained in the more complex hydrides, where HCF oxidizes selectively Pb–Pb bonds leaving the Pb–H bonds unaltered.

The slower reaction rate  $[\text{Fe}(\text{CN})_6]^{3-}$  towards THB,  $\text{PbH}_4$  and Pb–H containing species with respect to the oxidation rate of Pb–Pb bonds is probably the basis of the efficacy of this additive in the generation of  $\text{PbH}_4$ .

## 4. Conclusions

The most popular additive, the moderately oxidizing species  $[\text{Fe}(\text{CN})_6]^{3-}$ , has been under debate for many years [23,24,34,35]. In order to clarify controversial aspects related to mechanisms governing this popular analytical derivatization reaction it has been necessary to collect several different experimental evidences that integrated with thermodynamic considerations and literature information have made it possible to clarify a mechanism that has been controversial for a long time.

The first approach is aimed at clarifying the reaction of aqueous tetrahydridoborate with inorganic Pb(II) species in the absence of any additives. In this case, the reaction takes place in the pH range 1–8 and the inorganic aqueous lead substrates  $\text{Pb}^{2+}$  and/or  $\text{Pb}(\text{OH})^+$  are converted to solid, non-volatile species as hydrides and/or hydrido-metal complexes. These unstable species are formed in the early stage of reaction and contains, among the others, Pb–Pb and Pb–H bonds. In these conditions they evolve to form elemental Pb nanoparticles, the final product, without formation of volatile lead hydrides. In strongly alkaline conditions (pH > 12) inorganic Pb(II) is mostly present as  $\text{Pb}(\text{OH})_3^-$ , which are unreactive towards  $\text{BH}_4^-$ . However, if the concentration of lead is increased to the millimolar level or more the formation of elemental lead nanoparticles is observed. This occurs because the speciation of lead changes to PbO and lead polynuclear cationic species that are reactive towards  $\text{BH}_4^-$ . The experimental evidence collected in strongly alkaline conditions and high lead concentration [24,35] are therefore not representative of the reaction taking place in analytical conditions.

In the presence of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Pb}^{2+}$  and  $\text{Pb}(\text{OH})^+$  substrates are converted to  $\text{PbH}_4$  without any evidence of formation of solid species. Plumbane is formed by the direct transfer of hydride from borane to lead atom. Mechanisms of plumbane formation, which are based on the formation of borane-hexacyanoferrate complexes appear unlikely. One of the reasons arises from the evidence that the reaction rate of  $[\text{Fe}(\text{CN})_6]^{3-}$  with THB, under conditions similar to those occurring in CVG, is much slower than expected and more than 98% of  $[\text{Fe}(\text{CN})_6]^{3-}$  remains unreacted during the analytical derivatization. The hypothesis of a possible role played by borane-additive complexes [23] based on the kinetics reported by Freund [36], should be therefore revised in the light of the evidences herein reported.

The most likely role played by  $[\text{Fe}(\text{CN})_6]^{3-}$  must be searched in its

interaction with lead HMCs and polynuclear lead HMCs intermediates that are formed in the early stage of reaction of Pb(II) with THB. Most likely, it consists in the selective oxidation of Pb–Pb bonds. This action converts the solid, polynuclear lead HMCs to mononuclear fragments, which are converted to plumbane by the action of borane (reaction 8). The conversion of Pb(II) hydrides to more stable Pb(IV) hydrides promoted by  $[\text{Fe}(\text{CN})_6]^{3-}$  should be also considered according to literature information [47,51]. The evidence that the generation efficiency of plumbane in the presence of hexacyanoferrate(III) is almost quantitative [33], can be accounted for by a slower reaction rate of  $[\text{Fe}(\text{CN})_6]^{3-}$  with Pb–H bonds compared to Pb–Pb bonds.

Considering that the role played by additives in CVG of plumbane at trace level has never been clearly understood, the results of the present work may be helpful in understanding the role of the additives, other than hexacyanoferrate(III), that are used in CVG of plumbane. It seems now clear that, in general, the role played by additives can be of two types. In one case they will be able to favor the direct generation of  $\text{PbH}_4$  by preventing the formation of non-volatile intermediate lead hydrides, in the other case they will favor the formation of  $\text{PbH}_4$  from non-volatile intermediate lead hydrides.

The evidence that CVG of plumbane can be efficiently achieved by sequential and delayed mixing of reagents opens up to new strategies for the implementation of improved analytical methodologies, which are currently investigated in this laboratory.

## CRedit authorship contribution statement

**Emanuela Pitzalis:** Conceptualization, Methodology, Investigation, Data curation, Writing- Reviewing and Editing. **Beatrice Campanella:** Data curation, Investigation, Writing- Reviewing and Editing. **Rachele Bonini:** Conceptualization, Investigation. **Massimo Onor:** Conceptualization, Methodology, Investigation, Data curation, Writing- Reviewing and Editing. **Alessandro D'Ulivo:** Methodology, Investigation, Writing – original draft, Writing- Reviewing and Editing, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2023.341427>.

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