



## Review

# Mechanisms of chemical vapor generation by aqueous tetrahydridoborate. Recent developments toward the definition of a more general reaction model



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## ABSTRACT

A reaction model describing the reactivity of metal and semimetal species with aqueous tetrahydridoborate (THB) has been drawn taking into account the mechanism of chemical vapor generation (CVG) of hydrides, recent evidences on the mechanism of interference and formation of byproducts in arsane generation, and other evidences in the field of the synthesis of nanoparticles and catalytic hydrolysis of THB by metal nanoparticles. The new “non-analytical” reaction model is of more general validity than the previously described “analytical” reaction model for CVG. The non-analytical model is valid for reaction of a single analyte with THB and for conditions approaching those typically encountered in the synthesis of nanoparticles and macroprecipitates. It reduces to the previously proposed analytical model under conditions typically employed in CVG for trace analysis (analyte below the  $\mu\text{M}$  level, borane/analyte  $\gg 10^3$  mol/mol, no interference). The non-analytical reaction model is not able to explain all the interference effects observed in CVG, which can be achieved only by assuming the interaction among the species of reaction pathways of different analytical substrates. The reunification of CVG, the synthesis of nanoparticles by aqueous THB and the catalytic hydrolysis of THB inside a common frame contribute to rationalization of the complex reactivity of aqueous THB with metal and semimetal species.

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**Abbreviations:** ABC, analyte–borane complex intermediate; B–H, all species containing B–H bonds, including  $[\text{BH}_4]^-$  and hydridoboron species formed by  $[\text{BH}_4]^-$  hydrolysis; CVG, chemical vapor generation; DART, direct analysis in real time; GC–MS, gas chromatography mass spectrometry; THB, tetrahydridoborate ( $-1$ ),  $[\text{BH}_4]^-$ ; TDB, tetradeuteridoborate ( $-1$ ),  $[\text{BD}_4]^-$ .

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## 1. Introduction

Chemical vapor generation (CVG) of volatile species by aqueous tetrahydridoborate (THB) was first applied by Braman and coworkers, about 45 years ago, in the determination of Hg, As and Sb by atomic spectrometry [1,2]. Since that time, CVG dramatically increased in popularity and it has been widely employed in analytical atomic and mass spectrometry for the determination and speciation of trace elements, mainly Hg and the hydride forming elements As, Sb, Bi, Se, Te, Ge, Sn, Pb, and, more recently, also to Cd and Zn and several other transition and noble metals [3–6].

The investigation of the mechanism of CVG of volatile hydrides requires the adoption of model analytes which forms stable volatile molecular hydrides, because it is of obvious importance in the elucidation of the reaction pathways through which hydrogen atoms are transferred from the reaction environment (borane + solvent) to the analytical substrate then to final volatile hydride. Studies dedicated to the mechanism of formation of volatile hydrides by aqueous THB and other boranes have been recently performed with the aim to clarify controversial aspects and erroneous concepts in CVG [7–13]. The results of part of these studies allowed to describe a mechanism which is valid under analytical reaction conditions, that is analyte at trace level in pure aqueous solution and borane in strong excess ( $>10^3$  mol/mol), in the absence of foreign species other than the acid employed for pH adjustment. The proposed mechanism of CVG of volatile hydrides under analytical conditions has been summarized in reaction schemes, which could be considered valid also for transition and noble metals (see Fig. 7 in ref. [12] and Fig. 4 in ref. [13]). The key points of the proposed analytical mechanisms of CVG are represented in Scheme 1 and they can be summarized in the following points:

- i) Volatile hydrides are formed from direct transfer of hydrogen from borane species, B-H, to analyte atom, E, of the analytical substrate,  $EL_n$  (L is a ligand:  $OH^-$ , halogen ion,  $RS^-$  etc.)
- ii) The hydrogen transfer takes place through an analyte–borane complex, ABC;
- iii) The final volatile hydrides,  $EH_n$ , are formed stepwise and pass through the formation of intermediate hydrido–metal complexes.

Depending on the stability of the final hydride,  $EH_n$ , it can decompose giving the element in the zerovalent state, in some cases free atoms, which can aggregate giving nanoparticles and macroprecipitates. In the simplified scheme it has been omitted that, in general, also the instability of the intermediate hydrido–metal complexes could give origin to the element, nanoparticles and macroprecipitates, and it cannot say whether the final hydride is really formed or not, in the absence of direct evidences. The analytical mechanism, as the one depicted in Scheme 1, mainly concerns with the mechanism of hydrogen transfer from the reaction environment to the analytical substrate and disregards the cross-reaction of intermediate hydrides (hydrido–metal complexes), among them, and with analyte and final hydride. Even if the analytical mechanism has an applicability which is limited to CVG in almost ideal conditions, it is useful for the rationalization of the field and it would

contribute, hopefully, to minimize the propagation of erroneous concepts.

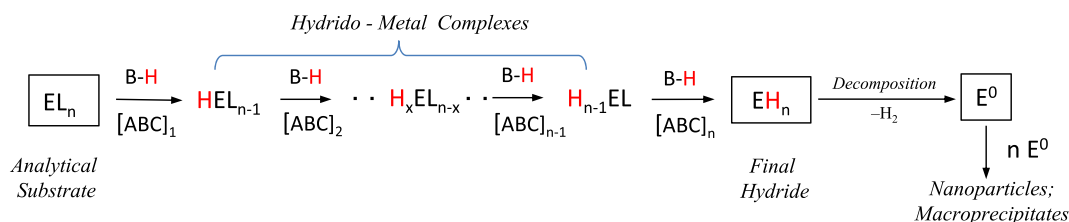
The reaction system, which is essentially based on the aqueous phase reaction of THB with metal and semimetal species, has found application in several different fields other than CVG atomic spectrometry for trace analysis of metal and semimetal species [3,4]. Two important fields are the use of aqueous THB for the synthesis of nanoparticles of metal and semimetals [14], and the production of hydrogen from the hydrolysis of THB catalyzed by metal nanoparticles [15,16]. The formation of metal nanoparticles or finely dispersed metals is also at the origin of severe interference in trace element determination by CVG atomic spectrometry [3]. It is reasonable to argue that the chemical pathways leading toward the generation of many different reaction products and interactions are part of a more general reaction system which can be selectively driven by a careful choice of experimental parameters. The idea to approach the definition of a reaction model that is more general than the analytical CVG mechanism [7,12,13] has been stimulated by some recent evidence on generation of arsanes which have been developed with the aim to understand how the ideal mechanism of analytical CVG and hydrogen transfer could be perturbed either by approaching quasi synthetic condition or in the presence of interferences [17,20].

The aim of the present review is to approach the definition of a reaction model for aqueous THB + metal or semimetal species the meaning of which expands beyond the field of analytical CVG for trace analysis. The definition of a more general reaction model has been achieved by integrating and discussing the present state of knowledge on analytical CVG with the recent evidences on mechanisms of CVG [17,18,19,20] and with other evidences reported in the literature on the synthesis of nanoparticles by aqueous THB and their application to catalytic hydrolysis of THB for hydrogen production.

## 2. Reaction products of THB with simple metal and semimetal aqueous species

### 2.1. CVG of metals

CVG of metals was firstly developed for the determination of Cu, Ag, Au and Zn [21,22] and it has been subsequently expanded to many other transition and noble metals [4,23]. Reaction products arising from CVG of transition and noble metals under analytical conditions are difficult to identify due to their instability and reactivity. However, experimental evidences reported that aqueous phase free atoms of Ag, Pd, and Cu have been detected in the solution following THB reduction of their ionic forms [24,25]. Similarly to mercury,  $Cd^{II}$  is reduced by  $NaBH_4$  to  $Cd^0$  and free cadmium atoms could be detected by AAS using a quartz cell at room temperature [26,27], but depending on the nature of surface material of chemical reactor also molecular cadmium species, assumed to be cadmium hydride, could be generated in addition to cadmium free atoms [27]. The nature of molecular volatile species detected by atomic and mass spectrometric techniques coupled with CVG of transition and noble metals remained unknown for a long time. Only recently the volatile species produced in the CVG of Ag [28] and Au [29] have been identified to be nanoparticles containing Ag and Au, respectively.



Scheme 1. Mechanism of CVG by aqueous THB, under analytical conditions and in the absence of interference.

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