Mechanism of Chemical Vapour Generation Using Tetrahydroborate(III) Derivatization

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Chemical vapour generation (CVG), by aqueous tetrahydroborate(III) (THB) derivatization, is one of the most powerful and widely employed methods for trace and ultra trace element determination and speciation in analytical chemistry. Fundamental aspects dealing with the mechanisms involved in CVG have scarce relevance in comparison with analytical applications and developments. Moreover, the analytical community has disregarded most of the experimental evidence relating to the chemistry of borane complexes that have been reported in the fundamental chemistry literature in the past years. These are probably the reasons for which CVG is still dominated by erroneous concepts which have been disseminated and consolidated within the analytical scientific community over the course of many years. The overall approach to CVG has thus remained completely empirical, which hinders the possibilities for further developments.

This presentation reports a discussion devoted to clarification of most controversial aspects of CVG. The discussion is based on the present status of knowledge [1-5], which results from the survey of fundamental chemistry literature (1950-1985) and recent dedicated experiments. In particular there will be discussed the following topics:

(i) Mechanism of hydrolysis of THB. The hydrolysis of THB takes place stepwise and the four hydrogen atoms bound to boron are lost with different reaction rates. Simultaneously, intermediate borane complexes containing three, two and one B-H bond (e.g. H$_2$O-BH$_3$, H$_2$O-BH$_2$OH, H$_2$O-BH(OH)$_2$) are sequentially formed. Deuterium labeled experiments indicates that molecular hydrogen is formed directly from borane complex decomposition without the formation of atomic hydrogen.

(ii) Mechanism of CVG. Deuterium labeled experiments indicates that hydrogen is directly transferred from boron to analyte atom. The intermediate borane complexes formed during THB hydrolysis still maintain the potentiality to perform derivatization reactions in CVG. Some of them are resistant to acid hydrolysis and can perform the derivatization in strongly acidic media.

(iii) Reaction model of general validity for CVG. The model is based on experimental evidences indicating the formation of complex intermediate between the analytical substrate and borane/hydroboran species (ABC: Analyte-Borane Complex). The hydrogen is then directly transferred from boron to analyte atom via intramolecular reaction taking place in ABC intermediate. In the case of multiple transfer of hydrogen atoms from boron to analyte atom (final hydride molecule contains two or more hydrogen atoms) the mechanism is stepwise and the hydrogen atoms in the final hydride come from different borane molecules.

References