## Mechanistic Aspects of Chemical Vapor Generation of Volatile Hydrides for Trace Element Determination

Aqueous phase chemical vapor generation (CVG) by derivatization with borane complexes, coupled with atomic and mass spectrometric detection techniques, is one of the most powerful and widely employed methods for determination and speciation analysis of trace and ultratrace elements (viz. Ge, Sn, Pb, As, Sb, Bi, Se, Te, Hg, Cd and, more recently, several transition and noble metals). Thousands of research papers and many regulated analytical methods are based on CVG. However, since its inception more than 35 years ago, the application and validation of CVG to many different analytical targets has been the prevailing focus of "research," whereas only limited efforts have been dedicated to clarification of the mechanistic aspects of the reactions. Analytical 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 possibilities for further development.

A rationalization of the field based on a more rigorous scientific approach appears to be necessary. The aspects requiring rationalization, which form the objectives of this project, can be classified as follows: mechanism of hydrolysis of borane complexes, mechanism of hydrogen transfer from the borane complex to the analytical substrate, and mechanism of action of additives commonly employed in analytical applications of CVG. Enhanced comprehension of these three different mechanisms and their mutual influence will provide the tools to explain the reactivity of a CVG system.

At present, there are essentially two main sources of information useful for comprehension of the mechanistic aspects of CVG. The first is represented by the fundamental data and experimental evidence relating to the chemistry of borane complexes that has been collected and reported in the literature in past years (1950–1980); regrettably, the analytical community has disregarded most of this fundamental literature. The second source is represented by the most recent experimental evidence specifically devoted to clarification of the mechanism of CVG (the past 10 years of work). The combination of these two major sources of information should make possible the rationalization of the mechanistic aspects of CVG, and will hopefully provide an impulse for further development in the field.

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## Assessment of Theoretical Methods for the Study of Reactions Involving Global Warming Gas Species Degradation and Byproduct Formation

Experimental techniques have always been used to study the thermodynamics and kinetics of chemical reactions. However, due to the explosive growth of computational power, quantum mechanical methods (semiempirical, ab initio, and density functional) have been found to be useful for these studies. Some researchers have also developed more adapted procedures using ab initio and density functional methods for studies.

Since global warming is a major concern, various studies are exploring the reactions involving global warming gas species degradation and byproduct formation. The aim of this new project is to carry out a critical analysis of the theoretical methods used to investigate these reactions and to assess to what extent the methods used are suitable in the predictions of thermodynamical parameters such as standard enthalpies, entropies, and heat capacities, and kinetics parameters such as activation energies and rate constants.

One of the outcomes of this project is to help researchers decide about the most promising method/methods in their future investigations.

The objectives of this project are as follows:

- to review the quantum mechanical methods that have been used to investigate reactions involving global warming gas species degradation and byproduct formation
- to assess the performance of the methods used by comparison with experimental data

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