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TRENDS

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Chemical vapor generation: are further advances yet possible?

Vapor generation, for the purpose of analytical application, is a process wherein volatile or semi-volatile analyte species are generated from nonvolatile precursors (usually ionic, metallic or organometallic) to permit their subsequent transfer from a condensed phase to the gas phase for enhanced detection capability. Although generation may be mediated by both biotic (biological) and abiotic (chemical) processes, it is the latter that is recognized for analytical application and is the focus of this Trends article. Chemical vapor generation (CVG) encompasses many of the same principal routes for such synthesis as those found in nature, viz hydride generation, alkylation, halide generation, generation of metal carbonyls and of elemental vapors (such as Cd and Hg) [1]. There is a fundamental drive to undertake CVG as it confers significant advantages for analyses, including: (1) efficient matrix separation, which frequently leads to reduction of interferences and enhanced detection power; (2) high transport efficiency of the anlayte to the detector; (3) high selectivity, in some cases, to permit differentiation of chemical species of a particular element; (4) enabling use of gas phase separation methods (gas chromatography) for speciation analysis of a number of elements. A significant body of literature pertaining to CVG exists, as the technique has been in widespread use for nearly 30 years. Whereas the reader may consult [2] for a comprehensive classical perspective, the advent of new and different approaches [1], such as photochemical vapor generation, is just now being explored and, in combination with newer approaches to sampling, appears to offer a powerful new perspective to the field.

A resurgence of research interest in CVG, giving rise to an expansion of the scope of this technique to encompass an increasing number of analytes, as well as to exploration of alternative methodologies for their sampling, is underway. In the past decade, new approaches to CVG have arisen, such as UV alkylation [3]; new approaches to analyte preconcentration have been explored, including cryocondensation and trapping of volatile species in aqueous media [4, 5]; new and powerful sampling strategies, such as SPME [6, 7] and single droplet microextraction [8, 9], have been pursued; new insights into the mechanism of one of the oldest CVG techniques, hydride generation, have emerged [10], and the elemental coverage continues to expand [11, 12].

The sustained interest in CVG by atomic spectroscopists is driven by their quest for enhanced detection power. The majority of sample introduction strategies is currently based on aqueous solutions and, for those systems relying on the use of pneumatic nebulization for sample introduction, such as flame atomic absorption and most plasma-based techniques, the efficiency of transfer of analyte from the solution to the spectroscopic source rarely exceeds 1–5%. Herein lies the stimulus for undertaking CVG, the vapor form of the analyte being efficiently separated from the liquid phase and transported quantitatively to the source. It remains only to ensure that the vapor generation step itself is as efficient as possible. High generation efficiencies, achieved with aquo-ion reduction by sodium tetrahydroborate(III), can now be routinely implemented for Hg, As, Sb, Bi and Se, frequently rendering CVG of these elements the preferred methodology for their determination by atomic spectrometry [2]. However, hydride generation of other elements, such as Te, Ge, Sn, Pb, In and Tl, is less frequently employed because optimum reaction conditions are not as easily accomplished, and the preferred, inexpensive quartz tube atomizer used for atomic absorption detection systems suffers from inefficient atomization for these elements. More often, aqueous phase *ethylation* (as opposed to classical Grignard alkylation in non-aqueous media) is undertaken, not only for these particular elements, but because reaction conditions for ethylation are sufficiently generalized (pH 5 medium), many hydride generation reactions

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would be achieved using tetraethylborate if the reagent were comparably priced to tetrahydroborate(III) [1].

Of substantial significance is the recent expansion of CVG techniques to encompass hydride generation of noble and transition metals [11, 12]. Although neither their mechanism of formation nor the identity of the resulting species has been elucidated, Cu, Pd, Ag, Pt, Au, Co, Ni, Rh, Ti, Mn, Zn and Ir have been investigated. Generation efficiencies for these elements range from greater than 50% to less than 1%. As research in this field is comparatively only just emerging, the discovery of new species is commanding higher priority than their in-depth characterization and, as a consequence, only minimal analytical use of this information has been harnessed to date. As these systems become better characterized and the hydride generation efficiency improved, the methodology will be driven from one of curiosity to analytical application. Recent advances in our understanding of the hydrolysis of the tetrahydroborate(III) reagent and discarding of the concept of “nascent” hydrogen as the mechanism of analyte reduction [10] may serve to illuminate new approaches to hydride generation, explain the effects of complexation reagents in enhancing performance, and provide a unified approach to optimizing the generation of volatile species. The fundamental role played by numerous hydroboron intermediates formed during the derivatization process appears to be key in these interpretations.

Amongst the many methodologies noted above for effecting CVG, one of the most significant recent developments is the application of photochemical reduction and alkylation [3, 13]. Alkylation, as a method for CVG, became widespread when interest in the speciation analysis of trace metals emerged. The technique, inspired by synthetic organic chemists, was initially confined to non-aqueous media (Grignard reaction), but availability of sodium tetraalkylborates has permitted efficient alkylation reactions to be conducted in aqueous media. Photo-induced alkylation [3] and photo-reduction of valence states [13] are emerging as powerful alternatives to conventional CVG that potentially provide for wide multielemental coverage, including As, Bi, Sb, Se, Sn, Pb, Cd, Te, Hg, Ni, Co, Cu, Fe, Ag, Au, Rh, Pd, Pt, I and S; the full extent of which remains to be explored. It also remains to be seen whether the simplicity of this approach, a UV source and inexpensive low molecular weight organic acids as chemical reagents, will permit it to functionally and analytically out-perform current hydride generation and carbonylation methodologies.

Use of classical chelating agents to foster the formation of volatile metal compounds is also on the cusp of “rediscovery”. The vapor pressures of many stable carbamates, ketonates and crown ether complexes are sufficient to permit their high temperature gas chromatographic detection [14]; Be, Al, Cr, Ni, Fe, Cu, Co, Mg, Ca, Ba, Se, Mn, Zr, Hg, Zn, Ga, Rh, V, Th, U, Pb, Cd, Pt and numerous rare earth elements have been investigated using this approach. Although separation of the species was originally required because conventional GC detectors were non-specific, use of modern SPE and SPME [15, 16] collection media coupled with their thermal desorption and direct introduction into atomic spectroscopic detectors serves to make chelation-based metal volatilization attractive for future evaluation/applications.

CVG may be construed as only “half” of the analytical process; the generated vapor species need to be either transported directly to a detection system or first collected for subsequent detection. In many cases, direct transport is undertaken if (a) the amount content in the sample is sufficiently high to permit reliable quantitation of the analyte; (b) compounds co-generated or present with the analyte (such as hydrogen, boron hydride, water vapor or high sodium ion concentration during hydride generation) are compatible with the detection system, and (c) a detector is available (field analyses are generally not feasible). Direct detection manifolds have been simplified by use of combined reactor/spray chamber/gas-liquid separation units [11, 17]. Further enhancement in the signal-to-noise ratio can be secured by (selective) collection of the species prior to its introduction to the detection system, thereby minimizing dilution effects induced from the presence of co-evolved gases and other gases used to achieve phase separation and transport. Conventional hydride generation has likely derived greatest benefit from in situ trapping of the vapors in a heated graphite furnace, providing exceptional detection power which can be further incremented by incorporating the furnace as part of a tandem source when coupled with ICP-MS for detection [18]. More recently, solid phase extraction and stir bar sorptive extraction techniques have begun to play larger roles in this field [15] as they potentially provide for some of the lowest limits of detection achievable with atomic spectroscopy [6]. Single droplet microextraction techniques should also be mentioned, although they are not as robust to work with [8, 9]. Cryogenic trapping also accomplishes the required goals, analyte enrichment and solute band concentration. Typical trapping temperatures are in the range −150 to −196 °C, obtained with liquid nitrogen cooling. This approach may be used strictly for sampling and then coupled to a separation system (typically for cryofocusing GC) [6] or used as its own first-order separation device where, with programmed heating, the analytes desorb from the trap in accordance with their boiling points [4, 19]. One of the main advantages of the cryotrapping technique is that unstable/reactive species do not come into contact with any liquid or solid sorbent materials, significantly reducing the possibility of their alteration/decomposition. A major impediment to its more widespread adoption, of course, is its bulkiness and the need to handle cryogenic liquids.

A collection/enrichment technique that has not yet been adequately characterized, but raises interest from many fundamental viewpoints, is the sequestering of vapor phase analytes in water [20]. In contrast to classical absorbing media, consisting of solutions of silver nitrate, dithiocarbamate or KI [2], water has recently

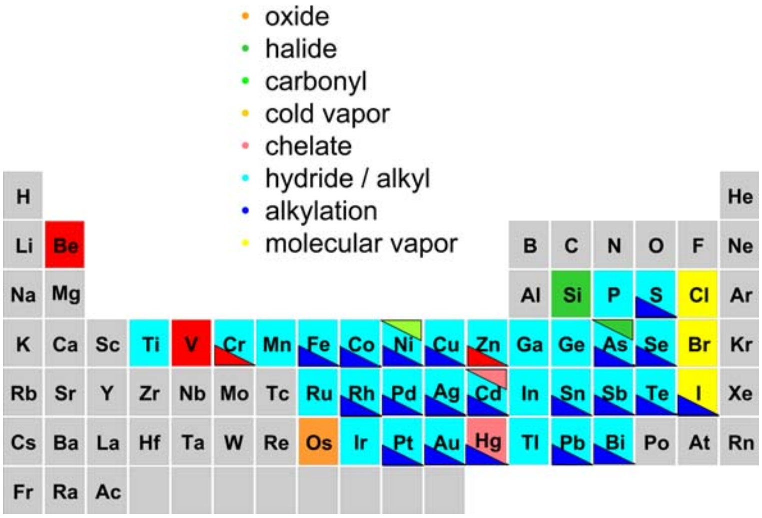

Fig. 1 Periodic Table of the elements indicating those that can be volatilized at atmospheric pressure and room temperature as: *green* fluoride, *red* chelates, *yellow* cold vapor, *light green* carbonyl, *orange* oxide, and *blue* hydrides

been successfully used to collect elemental Hg and Cd as well as other noble metal species arising from CVG. However, its capacity to do so is restricted by the solubility limit of the gaseous species (as opposed to collection via decomposition and formation of a soluble salt or complex). It is interesting to note that atomic Cd, in addition to the well-known case of atomic Hg, can be collected and recovered as such from water, permitting its concentration to be achieved following CVG.

The field of CVG for elemental and speciation analysis is broad and continues to evolve with the discovery of new species and methods for their generation, collection and detection. Several of the more classical techniques have become stagnant and are little used for analytical purposes, whereas others are experiencing a resurgence of interest. Developments are serving to significantly expand analytical capabilities in the fields of trace element analysis and organometallic speciation analysis. As illustrated by Fig.1, a major fraction of the metals and semi-metals throughout the Periodic Table can now be addressed by CVG techniques. Sustainable progress and expansion of interest in this science will depend on successful and widespread application of these new techniques to problem solving [21–24], identification of what these species are and development of a comprehensive fundamental understanding of their mechanism of formation. Without doubt, the years ahead hold great promise for continued advances in the field of CVG, the most exciting advances being those for which no framework of chemical principles currently exists that can be used to predict their discovery.

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