Atomic absorption spectrometry: vapor generation
Sturgeon, R.

National Research Council Canada   Conseil national de recherches Canada

Canada

R. Sturgeon

National Research Council Canada, Measurement Science and Standards, Ottawa, ON, Canada
Ph: 613 993 6395
Fax: 613 993 2451
Email: ralph.sturgeon@nrc.ca

Abstract

Generation of covalent hydrides and elemental mercury useful for enhancing the sample introduction efficiency and detection power of analytical atomic spectroscopy is described. Reduction using various chemical, thermochemical and photochemical techniques is considered and the resultant enhanced performance summarized along with a consideration of interferences and mechanisms of production and atomization. The techniques may be employed in batch, continuous and flow injection formats when interfaced to atomic absorption, emission, fluorescence and mass spectrometry detection platforms.

Introduction

The generation of gaseous analytes and their introduction into atomization cells offers several significant advantages over conventional solution-phase nebulization of samples[1]. These include the elimination of the need for a nebulizer, enhancement of transport efficiency (approaching 100%), and the presentation of a homogeneous vapor to the atomizer[2]. In addition to the widely practiced techniques of covalent hydride generation and mercury cold-vapor formation, which comprise the subject of this article, mention must also be made of the successful generation and introduction of volatile chlorides (Bi, Cd, Ge, Mo, Pb, Sn, Tl, As, and Zn), β-diketonates (Cr, Fe, Zn, Co, Mn, Cu, Ni, and Pb), and dithiocarbamates (Co and Cu) into atomization cells[3]. Additionally, ethylation, propylation, and phenylation (Sn, Pb, Se, and Hg) as well as carbonylation (Ni) reactions have been implemented[1,2]. Hydride generation (and cold-vapor) techniques significantly improve atomic absorption spectrometry (AAS) concentration detection limits while offering several advantages: (1)

separation of the analyte from the matrix is achieved which invariably leads to improved accuracy of determination; (2) pre-concentration is easily implemented; (3) simple chemical speciation may be discerned in many cases; and (4) the procedures are amenable to automation[4,5]. Disadvantages with the approach that are frequently cited include interferences from concomitant elements (notably transition metals), pH effects, oxidation state influences (which may be advantageously used for speciation) and gas-phase atomization interferences (mutual effect from other hydrides).

Hydride generation in AAS became popular after 1970 in response to a study by Holak[6], which demonstrated the analytical potential of this approach for arsenic. Since then, elements of groups IVA, VA, and VIA of the periodic table have been shown to form volatile covalent hydrogen compounds with sufficient efficiency to be of practical analytical use. These include arsenic, bismuth, germanium, lead, antimony, selenium, tin, tellurium, and to some extent, indium and thallium.

Although the determination of mercury in air by absorption spectroscopy was practiced before the advent of AAS, significant utilization of the cold-vapor technique arose during the 1960s (following the work of Hatch and Ott[7]) and has continued, essentially unaltered in procedure, to the present.

Hydride generation and cold-vapor techniques may be conveniently characterized by three steps: (1) generation of the volatile analyte; (2) its collection (if necessary) and transfer to the atomizer; and (3) decomposition to the gaseous metal atoms (unnecessary for mercury) with measurement of the AA response. Each of these steps will be briefly reviewed prior to considering the analytical performance of these techniques.

Formation of Covalent Hydrides and Mercury Vapor

Although several reactions have been utilized for the production of the hydrides, all rely on the formation of atomic hydrogen as a reductant. The classical metal–acid reaction employing Zn–HCl is limited to the generation of AsH$_3$, SbH$_3$, and SeH$_2$:

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2H \xrightarrow{E^{m+}} EH_n + H_2 \text{ (excess)} \quad (1)$$
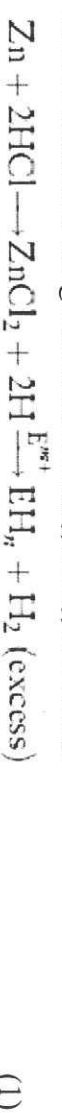
where E is the analyte element and m may or may not equal n. This system requires that these analytes be present in their lower oxidation states prior to reaction (otherwise they must be prereduced by addition of SnCl$_2$ and KI to the acidified sample). Zinc metal is then added and the hydrides, along with excess hydrogen, are evolved. The reaction is slow, difficult to automate, suffers from large blanks due to impurities in the zinc, and is inefficient as a result of incomplete reaction and/or entrapment of the hydride in the precipitated zinc sludge. These factors, along with the availability of more effective reducing agents (such as sodium tetrahydroborate) have served to all but eliminate use of this approach. Reduction to the hydride with sodium tetrahydroborate via reaction [2] is considerably more efficient:

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8H \xrightarrow{E^{m+}} EH_n + H_2 \text{ (excess)}$$

and can be used to generate the hydrides of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin[8]. It should be noted that the participation of 'nascent' hydrogen in reaction [2] is currently considered improbable[9] and the reaction illustrated in equation 2 is fundamentally simplified as many intermediate products of the acid catalyzed hydrolysis of tetrahydroborate are likely responsible for the reduction of metal ions in solution. Moreover, the mechanisms of chemical vapor generation are complex and involve multi-step consecutive additions of protons to intermediate species[9]. In addition to increased coverage, this reduction method is superior with respect to efficiency, speed, and reduced contamination. Reaction times are believed to be in the range of 10–30 s, although decomposition of the tetrahydroborate reagent is thought to be complete in a fraction of a second under acidic conditions[9]. Although initially added to acidified samples in the form of solid pellets, this reagent is now almost exclusively dosed into acidified samples as a 0.1–10% (m/v) solution, lending itself to ease of automation. The reagent is somewhat unstable and it is often recommended that it be prepared for storage by the addition of NaOH or KOH at concentrations of 0.1–2%. Others suggest that it be prepared fresh daily, filtered through membrane filters or stored in a refrigerator.

Most recently, amineboranes of the type $L\text{-}BH_3$ (where $L=NH_3$; *tert*-$BuNH_2$; Me_2NH; Me_3N) and sodium cyanotrihydroborate(III) ($NaBH_3CN$) have been tested[10] for efficacy of generation of elemental mercury and volatile hydrides of As(III), As(V), Sb(III), Sb(V), Bi(III), Se(IV), Se(VI), Te(IV), and Te(VI). All of the reductants are suitable for efficient generation of cold-vapor mercury but only some of the amineboranes are suitable for hydride generation, with Se(VI) and Te(VI) remaining unreactive. Reducing power follows the order: $NaBH_4 > H_3N\text{-}BH_3 > tert\text{-}BuNH_2\text{-}BH_3 > NaBH_3CN > Me_2HN\text{-}BH_3 > Me_3N\text{-}BH_3$. Of note is that the amineboranes and cyanotrihydroborate(III) provide for better control over interferences from Fe(III), Ni(II), Co(II), and Cu(II) than $NaBH_4$. These systems remain to be more thoroughly investigated, especially from an applications viewpoint. Although not directly the subject of this brief review, it is of interest to mention that recent work with trialkyloxonium tetrafluoroborates has shown successful application to the generation of a number of volatile anionic species, suitable for the determination of the halogens, sulfide, thiocyanate, cyanide, nitrate and nitrite[11].

Although aqueous systems are the most frequently encountered, the hydrides of some elements (antimony, lead, and tin) have also been generated directly from nonaqueous media (*N,N*-dimethylformamide, DMF) by the addition of $NaBH_4$/DMF solution as reductant. Hydrochloric acid remains the acid of choice, although H_2SO_4 and HNO_3 have also been used in generation media. Optimum acidity ranges depend on the element and are also often tailored to suit specific matrices, i.e., 1–9 mol l^{-1} for antimony, arsenic, and bismuth; 1–3 mol l^{-1} for germanium; 0.1–0.2 mol l^{-1} for tin and lead; 2.5–5 mol l^{-1} for selenium; and 2.5–3.6 mol l^{-1} for tellurium. Additional constraints enter into the generation of PbH_2 wherein oxidizing agents such as KCr_2O_7, H_2O_2, $(NH_4)_2S_2O_8$, $Ce(SO_4)_2$, or $KMnO_4$ are frequently added to the solution and believed to create lead(IV) intermediate in order to enhance the efficiency of conversion. The above reduction technique is not used with impurity, including the introduction of contamination (notably tin), interferences from concomitant transition metal ions and the evolution of excessive hydrogen (not considered a problem for AAS detection but potentially detrimental to plasma source atomic spectrometric techniques). Although infrequently used, electrochemical generation of the hydrides is also possible and has been applied to the determination of arsenic and tin in a batch approach and to antimony, arsenic, germanium, selenium, and tin using a flow-through electrolytic cell. The hydride is generated *via*

a multi-step process in the cathodic space of an electrolytic cell, with concurrent oxidation of water in the anodic compartment, as illustrated by the simplified reaction below[12]. Here, Me-E represents the reduced analyte element on the metallic cathode surface (Me):

$$Me\text{-}E + m\,e^- + m\,H_3O^+ \longrightarrow EH_m + m\,H_2O + Me \tag{3}$$

A high mass transfer rate of the analyte to the cathode surface is required for optimum efficiency. Batch sampling, continuous flow, and flow injection (FI) solution delivery coupled with batch reactors, thin-layer membrane separator designs, and tubular cells have been examined. Although no significant gain is evident with respect to interferences, minimization of contamination through elimination of chemical reducing reagent is possible, offering the lure of ever lower detection limits and green chemistry[13]. Electrochemical generation is reported to be less subject to oxidation state influence, exhibit greater freedom from interferences arising from concomitant elements, and liberate less excess hydrogen than homogeneous generation reactions based on tetrahydroborate(III)[12].

Thermochemical generation of hydrides appears feasible and has been utilized for the determination of arsenic species in the effluent from a liquid chromatograph. It is based on the injection of a thermospray aerosol into a methanol/oxygen flame where pyrolysis of the eluate occurs with subsequent thermochemical derivatization of the analytes and their transfer to a cool hydrogen-rich H_2/O_2 diffusion flame for atomization/AAS detection[14]. More recently, photo-induced generation of the hydrides has been reported utilizing UV-irradiation of the sample in an aqueous medium spiked with low molecular weight acids such as formic, acetic, malonic, etc[15-17]. The efficiency of the process is greater than 70% for Se and, depending on the species in solution, radical reactions can give rise to various products, including the simple hydrides or alkylated derivatives[18], as outlined below:

$$4RCOOH + Se(IV) \xrightarrow{h\nu} CO_2 + R_2Se$$
$$+\, 2RH + H_2 \quad (R = C_nH_{2n+1},\ n = 0,1,2) \tag{4}$$

It is self-evident that use of formic acid gives rise to the hydride species. Early results suggest that a number of elements are amenable to such a reaction, including As, Pb, Hg, etc. Cold-vapor AAS (CV-AAS) occurs in a manner similar to hydride generation AAS in that elemental mercury is formed in solution by reduction to Hg^0 followed by transport to and detection in an absorption cell. Simple first-order speciation of this element may be achieved using $SnCl_2$ under acidic conditions to selectively reduce inorganic mercury, and under basic conditions in the presence of copper (II) ion to reduce both inorganic and organomercury compounds. Until recently, tin (II) chloride solution (5-10% m/v) was almost exclusively used for the reduction of mercury. Currently, $NaBH_4$ is finding increasing application for this purpose and it has been suggested that selective reduction of inorganic mercury can be achieved using $SnCl_2$ at basic pH followed by subsequent reduction of organomercury compounds in the same solution by addition of $NaBH_4$[19]. This latter reagent also presents the advantage of faster liberation of the mercury from the solution phase and, in some cases, reduced interferences. Sodium tetrahydroborate is also attractive because of its comprehensive nature in that generation of mercury as well as all other covalent hydrides of interest can be accomplished in the same reaction vessel.

Vapor Generator

Hydrides

The hydride that is formed is flushed from the generating chamber with argon, helium, or nitrogen. There are essentially three methods used to generate hydrides with NaBH₄: (1) continuous systems where sample and reagent are pumped and mixed in a continuous fashion and then passed to some type of gas–liquid separation device; (2) batch systems, wherein a pellet of NaBH₄ or an aliquot of the reductant solution is added to the sample from which the volatile products are purged with a flow of transfer gas; and (3) FI systems in which discrete volumes of sample are merged with flowing streams of acid and/or reductant. These three arrangements are illustrated in Figure 1. Although automation is easily implemented and precision of measurement is often improved with continuous sampling as a result of the steady-state signals, this approach is at present little used with the AAS detection mode. Mixing coils, frequently inserted into flowing reaction systems, are useful only in that they aid in the phase separation of the hydride prior to entry into the actual gas–liquid separator. Such coils are generally not needed to increase the reaction time and in some cases have been shown to have a detrimental effect in that an enhancement in interference is observed. Gas–liquid phase separators have included simple arrangements, such as that illustrated in Figure 1, in addition to various hydrophobic membrane-based systems which provide for dry gas streams as well as shorter response and memory times.
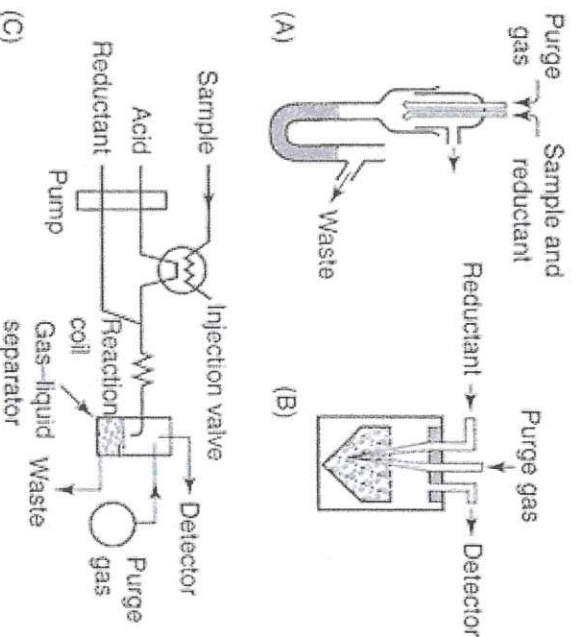
Figure 1
Hydride generation approaches: (A) continuous generation; (B) batch generation; and (C) flow injection.

(A)

Purge gas Sample and reductant

Waste

(B)

Reductant Purge gas

Detector

(C)

Sample

Acid

Reductant

Pump Injection valve

Reaction coil

Gas–liquid separator

Waste

Purge gas

Detector

The hydride technique is an absolute procedure in that the measured response is directly proportional to the absolute mass of the analyte element and not to its concentration in the solution. In practice, an aliquot of acid is usually added to the batch vessel followed by an accurately dispensed volume of sample. Depending on the apparatus used, peak-height quantitation may exhibit some sample volume dependence but this is absent when signal integration is used. Most batch reaction vessels for the hydride technique accept a relatively large sample volume (1–50 ml) whereas online FI techniques are flexible in that variable sample loop

volumes or timed sample pumping can be used to deliver an almost continuous distribution of desired volumes (typically 0.1–10 ml). FI offers a number of distinct improvements over the batch technique, such as high absolute sensitivity, reduced sample and reagent consumption, reduced interference effects, ease of incorporation of elaborate sample pretreatment, high sampling frequency, and ease of automation. A singular disadvantage remains the small volumes which, compared with batch systems, result in inferior relative sensitivity. As this is more than compensated for by the greater freedom from interferences and high absolute sensitivity, FI techniques are to be preferred for the analysis of real samples.

The transient hydride plume produced by either the batch or FI approach may be directly transferred to the atomization cell because reduction reactions are sufficiently rapid. Alternatively, the hydride is frequently collected in a cold trap (usually a cryogenic U-tube filled with a suitable adsorbent that is subsequently warmed to desorb the analyte) connected to the generator via a CaCl$_2$ drying tube, absorbed in solutions of AgNO$_3$, Ag-diethyldithiocarbamate, KI/I$_2$, Ce(IV)/KI, and I$_2$ (for subsequent quantification by graphite furnace AAS), or sequestered directly in a preheated graphite furnace prior to atomization/quantitation. These latter schemes permit significant additional preconcentration factors to be achieved while often eliminating or minimizing interferences associated with the generation step (generation kinetics)[20]. Most recently, the application of solid-phase microextraction fibers has permitted sampling of the evolved vapors for subsequent desorption and introduction into suitable detectors (such as ICPs and EI-MS sources)[21].

Several new approaches to the generation of the hydrides have recently come to the attention of the analytical community. One utilizes an anion exchanger, in the tetrahydroborate form, packed as a bed in the liquid channel of a gas–liquid separation membrane cell. FI-pumping of an acidic sample through the cell results in the heterogeneous production of hydrides that are rapidly transferred to the measurement cell[22]. The extent of some interference effects is reduced with this arrangement.

Recently, attention has focused on taking advantage of the rapid generation kinetics of the tetrahydroborate-acid reduction reaction to expand the suite of elements amenable to hydride generation. These include the use of a moving bed generator as well as modified parallel path concentric and cross-flow nebulizers, as illustrated in Figure 2. Rapid interaction of sample with reductant, while providing for instantaneous gas–liquid separation achieved with these systems, offer the potential for reduction or elimination of interferences from concomitant species in solution[23]. Successful generation of a number of 'unconventional' volatile species by reaction of acidified sample solutions with sodium tetrahydroborate has now been reported to include (in addition to Cd and Hg and the classical hydride forming elements): Cu, Ag, Au, Zn, Ni, Pd, Rh, Pt, Ti, Ir, Mn, Co, Fe, and Cr. Little is known of these species, except that they are relatively unstable, requiring rapid gas–liquid or gas–solid separation techniques, and they appear to be molecular in nature[24]. The full scope of elements amenable to such reactions is currently unknown. Reported generation efficiencies range from greater than 50% to less than 1%. Only minimal analytical use of these approaches has been reported to date.
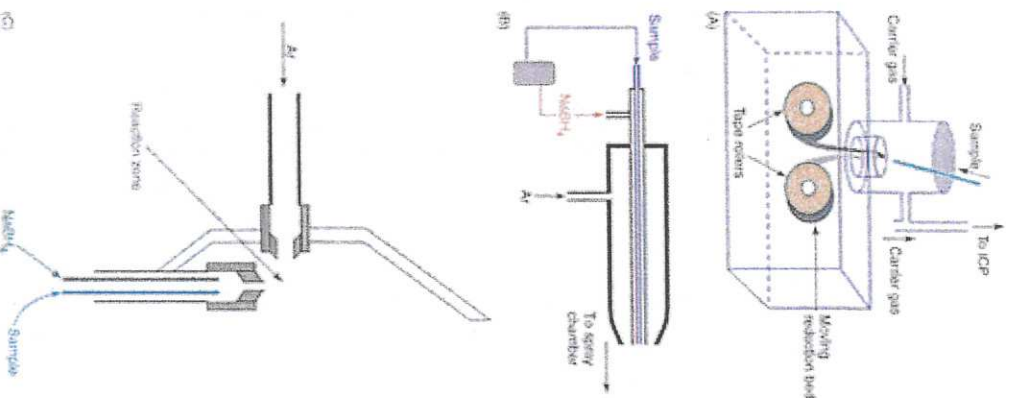
Figure 2

Hydride generation systems: (A) movable bed generator (Reproduced with permission from[25]); (B) modified Meinhard concentric nebulizer; and (C) cross flow nebulizer.

Combined generators, which are designed to take advantage of conventional introduction of liquid samples into atomization sources (such as the inductively coupled argon plasma, or emission or mass spectrometric detection of the analyte) along with simultaneous generation/introduction of the hydride forming elements, have also been proposed[26]. These are usually based on a conventional or modified spray chamber that permits introduction of reductant through an additional channel, permitting its interaction with the acidified sample aerosol.

Cold Vapor

Mercury is the only metallic element that is liquid at room temperature and possesses a significant vapor pressure. As a result of these unique properties, mercury can be determined without an atomization cell simply by reducing it to the elemental state and transferring it to the vapor phase within the optical path of a suitable detection system. Absorption is usually

measured at the 253.7nm resonance line. Similar to hydride generation, the majority of such determinations is usually accomplished using batch procedures, although FI systems are now enjoying more widespread usage. Figure 3 illustrates two mercury generation systems, one typical of that utilizing tin chloride or sodium tetrahydroborate as a chemical reductant and the other based on photochemical vapor generation using a low molecular weight organic acid (LMW) such as formic or acetic acid (2–5 % v/v) premixed with the sample and subjected to 254 nm radiation from a low power (3–20 W), low pressure mercury discharge lamp. Tin(II) chloride historically remains the preferred reductant; although NaBH$_4$ is a more powerful reducing agent, its use may increase the risk of certain interferences. These include excessive water droplet formation and carry-over as potential poisoning of amalgamation traps due to cogenerated hydrides if certain precautions are not undertaken. Use of 5 mol l^{-1} HCl in the presence of 200 mg l^{-1} Fe(III), an alkaline gas wash bottle to eliminate cogenerated SeH$_2$, a drying agent (Mg(ClO$_4$)$_2$) and, most importantly, ensuring that the amalgamation trap is below 100°C during collection (otherwise it suffers gradual poisoning) serve to minimize such problems. Helium is preferred over other gases as the most efficient sparging and transfer medium and an inline glass fiber filter is often used in place of the chemical desiccant (when SnCl$_2$ is used as the reductant) to remove any fine water droplets from the carrier stream (water vapor does not interfere with the absorption detection of mercury). Particular care must be taken in the selection of vessels and tubing in such apparatus due to the mobility and reactivity of mercury. Quartz ware and fluorinated ethylene propylene are often advised because they can be easily cleaned, are non-permeable, and exhibit little affinity for adsorption of mercury. Polytetrafluoroethylene (PTFE) tubing is superior to other materials for the transfer of mercury vapor.
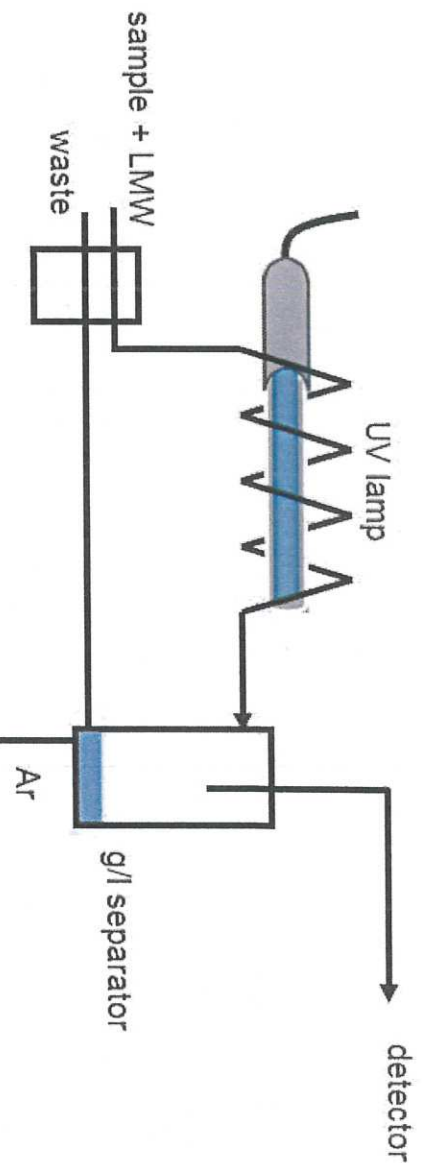
Reductant

Purge gas

Batch sample

Glass fiber filter

Heater

Au/Pt gauze

PTFE tubing

Heated quartz cell
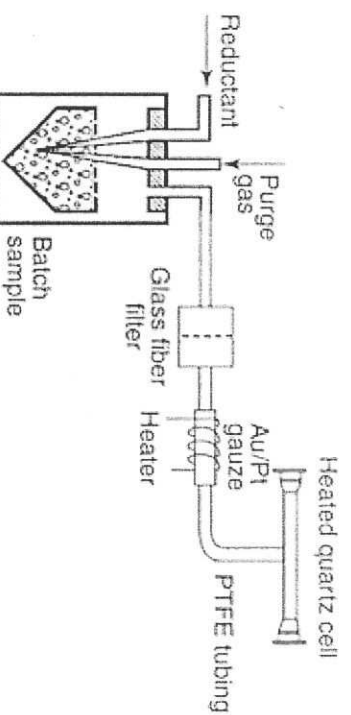
Figure 3
Typical cold-vapor mercury generation systems.

As with hydride generation, the evolved mercury vapor can either be transferred directly to the optical cell for measurement or trapped for later release. As the mercury is normally liberated slowly from solution over a period of 1–2 min, low intensity signals are generated; consequently, vapor trapping is frequently used to improve concentration detection limits for solution analysis. Enhanced separation and concentration of mercury is usually achieved by amalgamation on a noble metal trap, from which it is subsequently thermally desorbed (at 500–700°C). Currently, a gold–platinum gauze (90% Au, 10% Pt) is found to be most useful for this purpose because of its performance characteristics, which include high surface area, physical stability, thermal conductivity, and ease of cleaning. These properties lead to optimal signal reproducibility and generally an increase in sensitivity by 10-fold. Occasionally, two-stage gold amalgamation procedures have been utilized wherein the thermally desorbed mercury is recollected on a 'standardized' gold trap, which has been carefully calibrated, and is then desorbed into the spectrometer/detector. Water vapor that has collected on the first trap can be evaporated and interferences due to organic compounds (if air sampling has been used) that are oxidized during the first desorption, are thereby avoided. Alternatively, the generated mercury can be directed into a standard graphite tube atomizer (for GF-AAS), which has been lined with Pt gauze to effect *in situ* pre-concentration. Subsequent high temperature heating desorbs the mercury directly into the optical beam of the spectrometer, serving to further enhance sensitivity. The ease with which mercury ion is reduced in solution has led to the use of sonochemical[27], thermochemical[27] and photochemical[28] energy fields to efficiently generate the cold vapor from both inorganic and organometallic forms of the element.

Atomization and Detection

Hydrides

Conventional acetylene-based flame systems have found little use as atomization cells for hydrides. The relatively cool argon (entrained air)–hydrogen or simple air–hydrogen flame is advantageous as it exhibits low background absorption at lower wavelengths (15% at 193.7 nm). However, the excess hydrogen generated along with the hydrides often perturbs the flame, changing its composition and absorption characteristics, and the low kinetic temperature makes it more susceptible to interferences.

Currently, the most popular atomization source for hydride generation AAS is the heated quartz T-tube (typically 10 mm diameter×100–150 mm length). Both argon–hydrogen and air–acetylene flames have been utilized to heat open-ended silica tubes to which the hydrides are delivered in a stream of carrier gas from the generator via the central arm of the T. The quartz tube can also be heated electrically (700–100 °C) with the advantage of longer analyte residence time in the optical path and the possibility of obtaining the optimum atomization temperature for each element. Often, the tube is sealed with removable quartz windows at either end and fitted with nipples at the extreme ends as exits for the gas flow. These features result in improved sensitivity over the flame heated cells. Deterioration and aging of the interior surface of the quartz tube invariably occurs, leading to a decrease in sensitivity and precision. This has been attributed both to an irreversible devitrification of the quartz to a less satisfactory β-cristobalite structure and to contamination of the atomizer surface caused by deposition of liquid particles of the sample or small droplets that are carried from the generator into the tube. In the latter case, careful cleaning by soaking in 40% (m/v) HF often restores the sensitivity.

Also used for atomization sources are the flame-in-tube devices, in which the excess hydrogen generated during the reduction step is used to carry the hydrides to a T-shaped quartz tube. A small amount of oxygen or air is added to support the combustion of a small flame. Although more complicated than the simple quartz tube, this system does not exhibit any significant analytical advantages over the latter but has been found useful for mechanistic studies relating to atomization processes.

A recent, second generation modified flame-in-tube atomizer consisting of multiple miniflame ports located along the axis of the quartz tube provides for an extended region of active atomization to realize an enhanced absorption path length and reduced mutual interference effects from other cogenerated hydrides[29], as discussed later.

Continuously heated graphite furnaces have seen limited use as atomizers in which the hydride enters a preheated furnace (1800–2300°C) and is atomized during its transit time through the device. Although more bulky and difficult to operate, these systems offer a continuously clean and reproducible atomization surface, permit variable atomization temperatures to be used, and result in slightly improved limits of detection than those arising with the heated quartz tube. Tin, however, can suffer adsorption on any graphite transfer lines and reactions between water vapor, hydrogen, and graphite at high temperature give rise to increased background absorption.

An alternative system that is attractive for batch generation techniques, particularly FI-based approaches, is the use of the graphite furnace as both the pre-concentration cell and atomizer. The liberated hydrides are swept by a stream of inert gas into a warm (300°C) graphite furnace and directed onto the surface of a small (4 µg) previously reduced deposit of palladium which serves to catalytically decompose and trap the hydride. Following completion of the generation phase, the sequestered sample is atomized by cycling the furnace through a conventional high temperature heating program and the signal recorded. This approach permits additional pre-concentration to be achieved, is less prone to interferences, can be optimized for individual elements, and readily permits Zeeman-based background correction to be implemented.

Concentration detection limits are one to two orders of magnitude superior to all other hydride generation approaches[30]. *In situ* collection of generated hydrides has also recently been reported with the use of modified quartz tube atomizers, making provision for controlling the local oxidative and reductive atmospheres within the device during collection and atomization by varying the oxygen and hydrogen composition during these steps[31].

In addition to these 'online' atomizers, the graphite furnace has also been used in its traditional role as an offline device for the analysis of conventional liquid samples of sequestered hydrides. Aliquots of absorbing solutions used to tap the generated hydrides are injected into the furnace, atomized and quantitated in the usual manner.

Detection systems employed with hydride generation approaches are conventional AA spectrometers, usually fitted with intense electrodeless discharge or hollow cathode lamp sources. Quartz tube cells are of suitable dimensions to be compatible with the optical systems of all modern spectrometers. Background correction is usually achieved in double-beam optics using deuterium sources, and Zeeman-effect background correction can be implemented when the graphite furnace is used as the atomization cell.

Table 1 summarizes the limits of detection of a number of hydride forming elements reported for the various generation–detection methods. For comparison with continuous sampling techniques, a 10 ml sample volume has been assumed for *in situ* trapping in the graphite furnace (although larger volumes are easily accommodated) and a 500 µl volume for FI approaches. It is clear that, despite the small sample consumed for FI work, relative concentration detection limits are as good as those for continuous sampling. Additionally, 1000-fold improvements in detection power are readily achieved using *in situ* trapping.

Table 1 Concentration detection limits (3σ) for hydride generation and cold-vapor AAS techniques, ng ml⁻¹

Element	λ (nm)	GF-AAS (20µl)	Quartz tube, continuous	CF-AAS[a], in situ	Quartz tube, FI (500µl)
As	193.7	1.0	1.2	0.0043	0.40
Bi	223.1	0.5	0.3	0.0032	0.10
Ge	265.1	0.8	3.8	0.0017	—
Pb	283.3	0.3	0.6	0.0240	0.40
Se	196.0	1.5	2.7	0.0008	0.60
Sn	224.6	1.0	0.7	0.0037	0.30

Sb	217.6	0.8	0.7	0.0029	0.08
Te	214.3	0.5	2.3	—	0.20
Hg	253.7	1.0	0.02	0.002	—
		$(0.001)^b$			

[a]Based on a 10 µl sample volume.
[b]Gold trap amalgamation, 10 µl sample volume.

Cold Vapor

As the cold-vapor mercury sample is already in the atomic state, there is no need of an atomizer, *per se*. The vapor, transferred directly from the cell or desorbed as a plug from a heated amalgamation trap, is commonly swept into a moderately heated (resistance wound heating to 200°C) 10cm quartz T-tube located within the optical beam of a conventional AA spectrometer. Attenuation of an intense electrodeless discharge lamp line source at 253.7nm is used as a measure of the absorption. Alternatively, dedicated continuum source AA-based spectrometers fitted with long path absorption cells (30cm) are frequently used to increase sensitivity and detection limit.

Similar to hydride generation, graphite furnaces may be used both as the trapping medium and the atomizer for mercury. This may be accomplished by directing the evolved mercury from the generation cell onto an amalgamation medium (a reduced solution of gold or a gold–palladium gauze) inserted into the graphite tube for *in situ* preconcentration. Detection limits are generally improved threefold over conventional amalgamation trapping-quartz tube detection systems. Table 1 summarizes the reported detection capabilities for mercury using these various approaches.

Atomization Mechanisms

In argon/hydrogen diffusion flames and quartz tube atomizers, atomization of the hydrides is currently believed to proceed via interaction with free hydrogen radicals; oxygen also plays an active role. A cloud of hydrogen radicals is formed by reactions between hydrogen and oxygen:

$$H^\bullet + O_2 \longrightarrow OH^\bullet + O \quad (5)$$

$$O^\bullet + H_2 \longrightarrow OH^\bullet + H^\bullet \quad (6)$$

$$OH^\bullet + H_2 \longrightarrow H_2O + H^\bullet \quad (7)$$

The concentration of hydrogen radicals is several orders of magnitude higher than that of hydroxy radicals. In the quartz tube, this occurs either in a flame burning at the end of an oxygen delivery capillary (for a flame-in-tube device) or at the beginning of the hot zone for an externally heated tube (above 600°C). Only a small portion of the volume of the atomizer is

filled by the cloud, as determined by the gas dynamics, geometry of the tube and its temperature profile. The hydride is atomized within the radical cloud in accord with sequential collisions:

$$EH_x + H^\bullet \longrightarrow EH^\bullet_{x-1} + H_2 \qquad (8)$$

$$EH^\bullet + H^\bullet \longrightarrow E + H_2 \qquad (9)$$

The number of hydrogen radicals is primarily determined by the oxygen supply to the atomizer and, if insufficient, thermal decomposition of the hydride may occur (if the temperature is high) and lead to the formation of dimeric (and tetrameric for arsenic) species or, in the absence of hydrogen, to oxides, with consequent loss of sensitivity. Decreasing the inner diameter of the quartz tube serves to increase the radical cloud density but, as analyte atom attrition occurs predominantly by reaction with the quartz wall, the consequent less favorable surface area-to-volume ratio precludes any major enhancement in performance. Deterioration in sensitivity noted with tube aging may be accounted for by the formation of active sites, which serve to deplete the hydrogen radical concentration and/or scavenge analyte atoms.

Use of the multiple miniflame quartz tube atomizer[29] provides for a significant improvement in performance of this device. Recurrent analyte atomization occurs over the whole optical tube length, achieved by production of H-radicals at multiple points within the tube by oxygen microflames burning in the hydrogen-containing atmosphere. This feature serves to enhance the range of linearity in response to 200 μg l^{-1} for Se and Sb and 100 μg l^{-1} for As. A 10–100 fold improvement in tolerance to interferences from cogenerated analytes is also achieved.

It is believed that similar mechanisms are involved in the atomization from a graphite furnace operating in the direct transfer continuous mode of measurement. However, the probability of thermal dissociation increases substantially as the temperature of the source increases, with the result that radical mechanisms decline in significance above 2000°C. Atomization of the hydride elements trapped on reduced palladium within the graphite furnace appears to proceed at high temperature as a simple first-order desorption process from the surface of the deposit[30].

Interferences

Hydrides

The nomenclature and categorization of interferences arising with chemical vapor generation techniques has recently been summarized by D'Ulivo et al.[9]. Chemical interferences may occur in the liquid phase during formation and release of the hydride or in the gas phase during its transport to the atomizer or within the atomizer. The extent and severity of these interference effects vary widely and are dependent on the instrumentation and hydride generation system used. A 'physical' interference, often referred to as a kinetic interference, may arise as a result of a difference in the release rate of the hydride from solution due to a volume effect or perhaps to sample foaming. These interferences are only encountered in direct systems where the measurement is performed online; they do not occur when the hydride is collected.

Spectral interferences are essentially absent in hydride generation AAS because the analyte is completely separated from the sample matrix. Minor fluctuations that may occur in the baseline during sample introduction are easily compensated for with conventional background correction systems.

Although strictly 'chemical' in nature, oxidation state interferences are well recognized and generally easily dealt with. For elements of group IVA (germanium, tin, and lead), little is reported as to the influence of oxidation state on sensitivity, although it is clear that generation efficiency is remarkably enhanced for lead if reduction is performed in the presence of strong oxidizing agents (suggesting the formation of an intermediate Pb(IV) species, but likely implying an altered intermediate reductant based on tetrahyroborate[9]). For elements of group VA (antimony, arsenic, and bismuth), the sensitivity difference in peak-height mode of quantitation is less than twofold for the $+3$ and $+5$ oxidation states. As bismuth exists virtually in the $+3$ state, there is no concern. Under sufficiently acidic conditions, response from both arsenic (III) and arsenic (V) is the same. On- or offline pre-reduction of the sample with KI–ascorbic acid or KI–HCl is easily implemented for both arsenic and antimony if the sample preparation or dilution steps preceding measurement did not leave the analyte in the trivalent state. For the elements of group VIA (selenium and tellurium), only the $+4$ oxidation state is reactive and pre-reduction is required. This is often accomplished using hot 4–6 mol l^{-1} HCl. Advantage is frequently taken of the differential reactivity of the separate oxidation states of antimony, arsenic, and selenium to effect a first-order speciation of the element in the sample with respect to this parameter. This is easily implemented for antimony and arsenic simply by selectively generating the hydride from the $+3$ state at high pH and from both forms at low pH. It should be noted that pH also plays a significant role in the kinetics of hydrolysis of the tetrahydroborate species, thereby influencing the nature of the active reductant during the reaction[9].

It is also important that the various chemical species of the analyte be converted to a common form. Some of the organoforms of these elements commonly found in biological fluids and tissues are inert toward hydride formation (e.g., selenomethionine and arsenobetaine)[32] and care must be taken to ensure that the sample has been completely oxidized by, for example: treatment with peroxydisulfate at pH 2 for organoselenium compounds; alkaline peroxydisulfate for arsenic; and a mixture of $KBrO_3$–KBr–HCl for tin and bismuth (note that in all cases it is necessary to reduce all oxidation states 'back' to the lower valence state prior to analysis). Alternatively, sample analysis before and after extensive oxidative treatment again affords a further route for the methodologically defined speciation of the element. Additionally, methylarsonate and dimethylarsinate are reduced to methylarsine and dimethylarsine, respectively, and may be chromatographically determined following cryogenic trapping.

Few reports of the interference of acids (except HF) on the determination of the hydride forming elements have appeared. Only tin and lead exhibit a relatively strong pH dependence so they are normally determined in buffered media. In most cases, dilute hydrochloric acid ($<1 \text{ mol l}^{-1}$) is preferred, as higher concentrations give rise to increased contamination.

Of the common metallic elements, significant interferences are encountered in the presence of high concentrations of other hydride forming elements, iron, copper, nickel, cobalt, and the platinum group elements. This effect is not dependent on the analyte-to-interferent ratio, but rather on the concentration of the interferent in the analysis solution. Although several theories exist to account for these effects, the consensus is that preferential reduction of the interfering ion occurs and the resulting finely dispersed precipitate scavenges (and decomposes) the hydride formed in the secondary reaction. This explanation is supported experimentally, in that when concomitant element precipitation is avoided through the use of more concentrated acid solutions (5 mol l^{-1} HCl) and/or reduced concentration of tetrahydroborate reagent (0.5 versus 3%), the range of interference free determination can be enhanced 10–100 fold[33]. Other theories suggest that, even in the absence of precipitation, signal suppression can occur due to the formation of a

soluble complex between a lower than normal oxidation state of the interferent and the analyte. Excess NaBH4, serves to stabilize this intermediate. In the presence of high concentrations of other hydride-forming elements, competitive reactions between the different hydrides and possible loss of compound on metal precipitates may occur.

Gas-phase interference effects have been noted due to the mutual interference from the presence of other hydride-forming elements. As above, the extent of the interference is only dependent on the concentration of the interferent and not on the analyte-to-interferent ratio. As atomization of the hydrides occurs by collisions with hydrogen radicals, a 'radical population interference' may arise when an excess of cogenerated hydride depletes the hydrogen radical concentration to a level insufficient to completely atomize the analyte hydride. This theory is consistent with all observations made using heated quartz T-tube atomizers. Indeed, use of the multiple microflame quartz tube atomizer significantly reduces this problem, as noted earlier. Gas-phase interferences in the graphite furnace atomizer have been attributed to the formation of diatomic molecules between the analyte and cogenerated interferent and can be eliminated by use of high temperature.

A number of approaches have been taken to minimize or eliminate interferences. These include: increasing the acidity of the sample solution; reducing the concentration of the tetrahydroborate reagent; adding chelating or complexing agents to the solution (1-cysteine and l-cystine are particularly attractive[34]); the addition of interference releasing elements such as iron, tellurium, and copper, and the pre-separation of the analyte from the matrix.

FI techniques are particularly attractive for implementing such procedures[35], as they conveniently allow for rapid, elaborate sample pretreatment with minimal risk of increased contamination. This includes the online oxidation and pre-reduction of various chemical forms of the analyte, the addition of releasing or masking agents, as well as the separation of the analyte from major matrix components by ion exchange.

Cold Vapor

No spectral interferences occur with the cold-vapor technique; water vapor does not absorb at the 253.7nm line but water droplets carried into the cell may result in source attenuation. As a consequence, the cell is often operated at 200°C to prevent condensation.

Chemical interferences occur infrequently but include silver, arsenic, copper, iodine, antimony, and selenium. Tolerance to all these species except iodine and selenium is higher when $SnCl_2$ is used as the reductant as compared to NaBH4. Interference by platinum group metals using NaBH4 reductant is similar to that encountered with the hydride forming elements. Species containing sulfydryl groups retard the release of mercury from the sample but this interference effect is eliminated with amalgamation and/or signal integration. Organomercury compounds can be conveniently pre-oxidized using $KBrO_3$–KBr–HCl reagent prior to tetrahydroborate reduction.

Partial or complete poisoning of the amalgamation trap is more likely to occur when NaBH4 is used as a reductant and the precautions outlined earlier are not adhered to. Frequent cleaning in nitric acid minimizes this problem.

Applications

Hydride generation techniques are superior to direct solution analysis in several ways. However, the attraction offered by enhanced detection limits is offset by the relatively few elements to which the technique can be applied, potential interferences, as well as limitations imposed on the sample preparation procedures in that strict adherence to valence states and chemical form must be maintained. Cold-vapor generation of mercury currently provides the most desirable means of quantitation of this element, although detection limits lower than AAS can be achieved when it is coupled to other means of detection (e.g., nondispersive atomic fluorescence or microwave induced plasma atomic emission spectrometry).

Applications of both vapor generation techniques have been widespread in that waters and effluents, metallurgical, clinical, biological, agricultural, geological, and environmental samples have all been analyzed at both the trace and ultratrace levels for these analytes. The reader is referred to the Further Reading (?) section for an extensive compilation of specific applications. Currently, detection power is primarily limited by reagent contamination. Progress in the widespread implementation of FI techniques, which feature online sample preparation and pretreatment capabilities as well as capabilities for rapid automation, should facilitate a further revolution in the use of vapor generation techniques in atomic spectroscopy as will, without doubt, the further development of photochemical vapor generation techniques[36,37].

Article History

R. Sturgeon has updated the text and references to this entire article and modified Figure 3, December 19, 2012.

References:

ATOMIC ABSORPTION SPECTROMETRY | Principles and Instrumentation; ATOMIC ABSORPTION SPECTROMETRY | Interferences and Background Correction; ATOMIC ABSORPTION SPECTROMETRY | Flame; ATOMIC ABSORPTION SPECTROMETRY | Electrothermal.

1. Dědina J.; Tsalev D. L. Hydride Generation Atomic Spectrometry; John Wiley: Chichester, 1995
2. Wu, P.; He, L.; Hou X.; Sturgeon, R.E., *J. Anal. At. Spectrom.* **2010**, 25, 1217-1246
3. Sturgeon, R.; Mester, Z., *Appl. Spectrosc.* **2002 56** () 2002A–2213A

4. Pohl, P.; Sturgeon, R.E., *Trends Anal. Chem.* **2010**, 29, 1376 - 1389

5. Nakahara, T., *Prog. Anal.l At. Spectrom.* **1983**, 6, 163–223

6. Holak. W., *Anal. Chem.* **1969**, 41, 1712-1713

7. Hatch, W.R.; Ott, W.L., *Anal. Chem.*, 1968, 40, 2085-2087

8. Thompson, K. C.; Thomerson, D. R., *Analyst* **1974**, 44, 595 - 601

9. D'Ulivo, A.; Mester, Z.; Sturgeon, R.E.; Wang, Q.; Welz, B., *Pure Appl. Chem.* **2011**, 83, 1283–1340

10. D'Ulivo, A.; Loreti, V.; Onor, M.; Pitzalis, E.; Zamboni. R., *Anal. Chem.* **2003**,75, 2591-2600

11. D'Ulivo, A.; Pagliano, E.; Onor, M.; Pitzalis, E.; Zamboni, R., *Anal. Chem.* **2009**,81, 6399-6406

12. Bolea, E.; Laborda, F.; Castillo, J.R; Sturgeon, R.E., *Spectrochim. Acta, Part B* **2004**, 59, 505 - 513

13. Zhang, W.; Yang, X.; Xue, J.; Wang, S., *J. Anal. At. Spectrom.* **2012**, 27, 928 - 936

14. Smichowski, P.; Madrid, Y.; de la Calle Guntinas, M.B.; Camara, C., *J. Anal. At. Spectrom.* **1995**, 10, 815 – 821

15. Guo, M.-M.; Sturgeon, R.E.; Mester, Z.; Gardner, G., *Anal. Chem.* **2003**, 75, 2092–2099.

16. Zheng, C.; Ma, Q.; Wu, L.; Hou, X.; Sturgeon, R. E., *Microchem. J.* **2010**, 95, 32 - 37

17. Zheng, C.; Yang, L.; Sturgeon, R.E; Hou, X., *Anal. Chem.* **2010**, 82, 3899–3904

18. Sturgeon, R.E.; Grinberg, P., *J. Anal. At. Spectrom.* **2012**, 27, 222 – 231

19. Zhang, Y.; Adeloju, S. B., *Anal. Chim. Acta* **2012**, 721, 22 – 27

20. Sturgeon, R.E; Gregoire, D.C., *Spectrochim. Acta, Part B* **1994**, 49, 1335 - 1345

21. Vercauteren, J.; Peres, C.; Devos, C.; Sandra, P.; Vanhaecke, F.; Moens, L., *Anal. Chem.* **2001**, 73, 1509 – 1514

22. Chuachuad, W.; Tyson, J.F., *J. Anal. At. Spectrom.* **2005**, 20, 282–288

23. Ding, W.-W; Sturgeon, R.E., *Anal. Chem.* **1997**, 69, 527–531

24. Feng, Y; Sturgeon, R.E.; Lam, J.; D'Ulivo, A., *J. Anal. At. Spectrom.* **2005**, 20, 255–265

25. Tian, X-D.; Zhuang, Z-X.; Chen, B.; Wang, W-R, *Analyst* **1998**, 123, 627–632

26. MacLaughlin, R.L.; ; Brindle, I.D., *Anal.l At. Spectrom.* **2002**, 17 1540–1548

27. Ribeiro, A.S.; Vieira, M.A.; Willie, S.N.; Sturgeon, R.E., *Anal. Bioanal. Chem.* **2007**, 388, 849 - 857

28. Vieira, M.A.; Ribeiro, A.S.; Curtius, A.J.; Sturgeon, R.E., *Anal. Bioanal. Chem.* **2007**, 388, 837 - 847

29. Matousek,T.; Dedina, J.; Selecka, A., *Spectrochim. Acta Part B* **2002**, 57 451- 462

30. Sturgeon, R.E.; Willie, S.N.; Sproule, G.I.; Robinson, P.T.; Berman, S.S., *Spectrochim. Acta Part B* **1989**, 44, 667 – 682

31. Kratzer, J., *Spectrochim. Acta Part B* **2012**, 71–72B, 40 – 47

32. Willie, S.N., *Spectrochim. Acta Part B* **1996**, 51, 1781 – 1790

33. S Welz, B.; Schubert-Jacobs, M., *J. Anal. At. Spectrom.* **1986**, 1, 119 – 124

34. Brindle, I.D.; Le, X-C., *Anal. Chim. Acta* **1990**, 229, 239 - 247

35. Welz, B.; Schubert-Jacobs, M., *At. Spectrosc.* **1991**, 12, 91 - 104

36. He, Y.; Hou, X.; Zheng, C.; Sturgeon, R.E *Anal. Bioanal. Chem.* **2007**, 388, 769 - 774

37. Zheng, C.; Ma, Q.; Wu, L.; Hou, X.; Sturgeon, R. E., *Microchem. J.* **2010**, 95, 32 - 37

Further reading:

Welz, B.; Sperling, M. *Atomic Absorption Spectrometry*, 3rd edn; Wiley-VCH: Weinheim, 1999

Journal of Analytical Atomic Spectrometry, annual updates sections covering: environmental analysis; clinical and biological materials; advances in atomic spectrometry and related techniques and industrial analysis.