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Insights into the mechanism of chemical vapor generation of transition and noble metals

Yong-Lai Feng,[b] **Ralph E. Sturgeon,**[*a] **Joseph W. Lam**[a] **and Alessandro D'Ulivo**[c]

[a] *Institute for National Measurement Standards, National Research Council Canada, Ottawa, Canada K1A 0R9*
[b] *Chemistry Research Division, Health Canada, Tunney's Pasture, Ottawa, Canada K1A 0L2*
[c] *Institute for Chemical and Physical Processes, Laboratory of Instrumental Analytical Chemistry, National Research Council of Italy, Research Area of Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy*

The mechanisms of chemical vapor generation (CVG) of transition and noble metals by reaction with tetrahydroborate(III) have been investigated in an effort to reconcile fundamental properties of compounds containing metal–hydride bonds with the experimental evidence collected in the present work and in the recent analytical literature on CVG. Silver, gold and rhodium were investigated in detail. Various materials constituting the wetted surfaces of the reaction apparatus (Ryton, glass, silanized glass) were examined for their effect on the overall process, as was the presence of surface-active agents (Triton X-100[TM], antifoam B). Two types of reactions contribute to the formation of volatile species. The first (primary reaction) occurs through homogeneous liquid phase reactions between aqueous analyte complexes (ML_n) and hydroboron species (BH_4^- and its hydrolysis products). The second (secondary reaction) is a surface mediated reaction between reaction intermediates, mostly formed in the primary reaction and chemisorbed by active sites on surfaces, and hydroboron species. The participation of active surface sites generally improves the efficiency of CVG compared with use of an inert surface, but this feature cannot always be usefully employed in analytical applications due to slow reaction kinetics producing memory effects. Reaction intermediates which can be classified as hydrido metal complexes, L_nMH_x, possess complex chemistry, making interpretation of experimental results difficult. Hydrido metal complexes, in addition to free atoms and nanoparticles, may constitute the volatile species leaving the solution and/or reaching the atomizer.

Introduction

Chemical vapor generation (CVG) of transition and noble metals opens a novel route for introduction of these elements into atomic spectrometric sources and can be accomplished by merging an acidic sample with tetrahydroborate(III) reductant solution.[1–19] An early investigation by Sanz-Medel *et al.*[8] on the generation of a volatile species of Cd by reduction of Cd(II) with sodium tetrahydroborate(III) in aqueous solutions containing vesicles of didodecyldimethylammonium bromide fostered studies by Sturgeon *et al.*[1–7] on the vapor generation of Cu, Au, Ag, Zn, Rh, Pd, In, Hg, Tl, Pb and Cd. These were supported by subsequent observations of Pohl and Zyrnicki[10–12] on the transport of volatile species of Co, Cr, Fe, Os, Rh, Ru and Ni to an ICP during hydride generation using a pneumatic nebulizer of the Meinhard type. Similarly, Wang *et al.*[16] studied the generation of Cd and Cu species using a movable reduction bed hydride generator. Volatile species of Ag, Cd, Au, Co, Cu, Ni, Sn and Zn have also been independently studied by others.[13,18,19]

The current study is divided into two parts. In the first, an effort is made to provide a general reaction scheme for CVG by presenting a survey and discussion of the information available in the fundamental chemistry and analytical literature. Despite relatively widespread investigations in analytical chemistry into CVG, there have been few attempts to reconcile the reported experimental results with the fundamental chemistry of hydrides of transition and noble metals. The most recent discussions and developments on the mechanisms of tetrahydroborate(III) hydrolysis and formation of classic hydride forming elements[20–23] introduce a new opportunity to revise the mechanism of CVG of metals, originally proposed as a two-step mechanism.[24] In the second part of this study, additional experiments on the CVG of transition and noble metals following their reaction with tetrahydroborate(III) reductant are presented to substantiate the proposed mechanism of vapor generation. The mechanism, whose scheme is of general validity for both metals and metalloids, proposes a multi-step process encompassing the formation of unstable hydrido metal complexes which may evolve to form the final products. The nature of the volatile species leaving the reaction solution or reaching the detector (presumably as a molecular hydride or hydrido metal complex, but possibly also as free atoms or nanoparticles) remains to be identified.

Experimental

Instrumentation

A PerkinElmer SCIEX (Concord, Ontario, Canada) ELAN 5000 ICP-MS was operated under conditions described in earlier work.[1] A modified parallel path Burgener nebulizer was used as the vapor generator[1] in which the aerosol gas channel (herein designated as the "shear gas") was concentric with both the sample and tetrahydroborate(III) solution channels. The nebulizer was mated to the spray chamber with the use of a standard commercial push-fit Teflon end cap. Two "demountable" double-pass spray chambers were used, consisting of either polymeric Ryton [poly(*p*-phenylene) sulfide] or glass. The glass spray chamber was fabricated in-house and was of the same dimensions as that of the commercial Perkin Elmer double-pass Ryton chamber. The inner glass tube (first

pass for aerosol) was mounted in place with the use of a Teflon bung, which permitted the spray chamber to be conveniently demounted, and fitted with inner glass tubes of variable dimensions as well as a standard Ryton inner tube. The commercial Ryton double-pass spray chamber was similarly demountable, in that the center tube was also maintained in place with a Teflon bung which permitted both the standard Ryton inner tube as well as various glass tubes to be inserted into the spray chamber. A "T" inlet for make-up gas was located at the outlet of each spray chamber and directly connected to the plasma torch, permitting independent optimization of the (make-up) carrier gas flow. The flow rate of Ar admitted to this inlet (herein designated as "make-up gas") was maintained using an external mass flow controller. Sample and reductant streams were introduced either in a continuous manner at a flow rate of 1.1 ml min^{-1} each, using a four-channel 12 roller Minipuls 2 peristaltic pump (Gilson, Middleton, WI), or the sample was added discretely, injected as an 80 μl volume using a loop inserted into the acidified sample steam. For this purpose, a flow injection manifold fitted with a manual metal-free injection valve for merging the loop contents with a continuous stream of reductant was used.

For some experiments, the interior of the glass spray chamber (and first pass inner tube) was silanized by rinsing with a 10% solution of dimethyldichlorosiloxane in toluene followed by drying at 150 °C.

Several experiments were performed with spray chambers in which a Nylon 6 mesh was inserted into either the inner glass or standard Ryton tube such that the mesh uniformly covered the inner wall of these tubes.

Reagents

Stock solutions (1000 mg l^{-1}, 99.99%) of Sb(III), Cu(II), Ag(I), Au(III), Cd(II), Ni(II), Pt(II), Rh(III), Co(II), Mn(II) and Pd(II) were obtained from SCP Science (Montreal, PQ, Canada). Working standards of lower concentration were prepared by dilution of the stocks using 18 MΩ cm deionized, reverse osmosis water (DIW) obtained from a mixed-bed ion-exchange system (NanoPure, Model D4744, Barnstead/Thermolyne, Dubuque, IA). High-purity sub-boiling distilled HCl and HNO$_3$ were prepared in-house and used for acidification of the working standards. A 1% (m/v) solution of sodium tetrahydroborate(III) in 0.001 M NaOH was prepared daily, or more frequently, if required. Both reagents were purchased from Alfa Aesar (Ward Hill, MA). Dimethyldichlorosiloxane was purchased from Pierce Chemical Co. (Rockford, IL). Triton X-100^{TM} was obtained from Sigma–Aldrich (Oakville, Ontario, Canada). Antifoam B agent was purchased from Mallinckrodt Chemicals (Phillipsburg, NJ). A nylon mesh (NITEX, 0.2 mm mesh dimension) was obtained from B. & S. H. Thompson & Co. Ltd, Montreal. All solutions were prepared in a clean room providing a class 100 working environment and glassware was soaked for at least 24 h in 1 M nitric acid and rinsed with DIW before use. Argon gas was obtained from Praxair (Mississauga, ON, Canada).

Procedures

Once the argon plasma was ignited and stabilized, the vapor generator was brought on-line, steady-state signals established using a 100 ng ml^{-1} multi-element feed solution, and the instrument peaked for maximum response. A number of variables were optimized, including the total aerosol and make-up gas flow rates, analyte and reductant solution flow rates, as well as acid and reductant concentrations. Data were manipulated using MS Excel and in-house software. A shear gas flow rate of 0.4 l min^{-1} was found to be optimal for the generation/separation of volatile species, which is clearly different from the typical conditions used for maximum aerosol generation efficiency employed with conventional pneumatic sample introduction.[1,24] With this system, almost no aerosol was introduced into the plasma, as evidenced by monitoring signals at m/z 75 and 77 in a hydrochloric acid medium. In order to ascertain that the generated signal was genuine, every signal obtained was compared with that arising from the introduction of a matrix matched blank solution and at least two isotopes of each analyte were used as confirmation of signal measurement, where available.
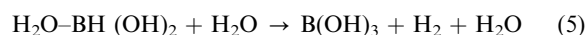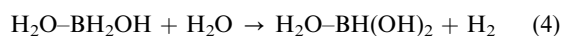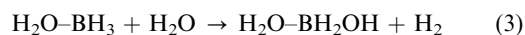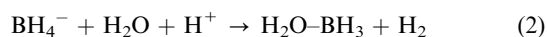
Results and discussion

Part 1

CVG of covalent hydrides. Chemical hydride generation with tetrahydroborate(III) is typically characterized by the following reaction:

$$BH_4^- + 3H_2O + H^+ \rightarrow B(OH)_3 + 4H_2 \qquad (1)$$
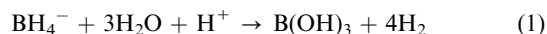
Reaction (1) is the result of a stepwise process passing through the formation of hydroboron intermediates[20,21,25] which can be represented, in pure aqueous solution, by the following equations:

$$BH_4^- + H_2O + H^+ \rightarrow H_2O–BH_3 + H_2 \qquad (2)$$

$$H_2O–BH_3 + H_2O \rightarrow H_2O–BH_2OH + H_2 \qquad (3)$$

$$H_2O–BH_2OH + H_2O \rightarrow H_2O–BH(OH)_2 + H_2 \qquad (4)$$

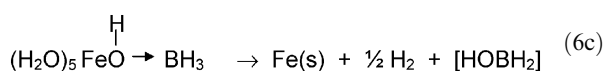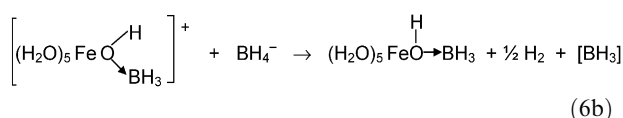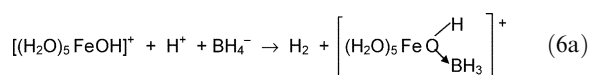$$H_2O–BH(OH)_2 + H_2O \rightarrow B(OH)_3 + H_2 + H_2O \qquad (5)$$

According to reaction conditions, pH, type of acid (AH) and the presence of ligand/donor species (L), many different types of intermediates can be formed:[20,21] $[LBH_3]^m$, $[L_2BH_2]^m$ and $[L_3BH]^m$, where L could be one or more among H$_2$O, NH$_3$, NR$_3$, OH$^-$, Cl$^-$, RCOO$^-$, RS$^-$, etc., and m ($m = 0, +1, -1$) is the charge on the hydroboron intermediate, which depends on the nature of the L group.

The decomposition of tetrahydroborate(III) in the pH range 3.8–14 is a second-order reaction having a rate constant (at 30 °C) of 1.22×10^8 mol^{-1} l min^{-1}.[26] The rate determining step is loss of the first hydrogen (reaction (2)). At pH ≤ 1, the overall rate of decomposition of tetrahydroborate(III) is considerably reduced by the formation of acid resistant hydroboron intermediates. The loss of the first hydrogen should be complete within a few microseconds of mixing with acid, in accordance with the second order reaction kinetics mentioned above.[21]

The mechanism of vapor generation for Hg and the classical hydride forming elements As, Sb, Bi, Sn, Se and Te is due to the reaction of one or more hydroboron species $[L_xBH_{4-x}]^m$ ($x = 0–3$, and the charge $m = 0, \pm 1$) with the analyte substrate at $-1 \leq$ pH ≤ 2.[21] From near neutral pH to strongly alkaline conditions, the BH$_4^-$ species play a dominant role in the generation of SbH$_3$, BiH$_3$ and SnH$_4$.[22] In any case, the formation of volatile hydrides is due to direct transfer of hydrogen from boron to the analyte atom, as indicated by experiments with deuterated reagents.[20,23] The successful generation of the final hydride is strictly related to the structure of both the hydroboron intermediate and of the analyte substrate.[20–22]

CVG of transition and noble metals. In the case of the transition and noble metals (M), their reaction with tetrahydroborate(III) in aqueous solution generates unidentified volatile species, which makes comprehension of the reaction mechanism quite difficult. It is well known that the final products are the reduced metals or metal borides, depending on the metal and on the experimental parameters, and that this reaction is widely employed for the preparation of nanoparticles of metals or metal borides.[27,28] This can be considered the result of a coalescence process, starting with the formation of free atoms in solution, as demonstrated by Panichev and

Sturgeon.[5] However, with vapor generation of transition and noble metals, the resultant species are not chemically stable in solution,[1–3] and thus extended reaction time leads to decreased product yield.[1,2] This is an important piece of evidence indicating that the volatile metal products are unstable or transient species arising from the interaction of hydroboron species, including BH_4^-, with metal ion species in aqueous solution, $[ML_n]^q$, where L = H_2O, OH^-, Cl^-, or any other suitable ligand present in the reaction environment, n is the coordination number of the metal and q is the charge on the metal complex. The free atom could therefore be one of the products arising from the chemical evolution of a precursor intermediate such as, for example, that proposed in the case of reduction of Fe(II) in aqueous solution:[28]

$$[(H_2O)_5FeOH]^+ + H^+ + BH_4^- \rightarrow H_2 + \left[(H_2O)_5Fe\underset{BH_3}{\overset{H}{\diagup}}O\right]^+ \quad (6a)$$

$$\left[(H_2O)_5Fe\underset{BH_3}{\overset{H}{\diagup}}O\right]^+ + BH_4^- \rightarrow (H_2O)_5Fe\overset{H}{O} \rightarrow BH_3 + \tfrac{1}{2}H_2 + [BH_3] \quad (6b)$$

$$(H_2O)_5Fe\overset{H}{O} \rightarrow BH_3 \rightarrow Fe(s) + \tfrac{1}{2}H_2 + [HOBH_2] \quad (6c)$$

In the case of Ni(II), Lugowska and Brindle[29] reported the formation of compounds of the type $(NiH_2)\cdot(Ni_2B)\cdot 2H_2O$ and $(NiH_2)(ONiH)_2B$. This indicates the presence of Ni–H, Ni–B and B–O–Ni–H bonds, which can be formed by reaction paths different from 6a–c.

Hydrido metal complexes of the type L_nMH have been widely investigated, as have metal polyhydride complexes, L_nMH_x.[30] In some polyhydrides the hydrogen atoms are bound to the metals as both M–H and $M(H_2)$, the latter being molecular hydrogen complexing the metal. The stability of hydrido metal complexes is strongly related to the nature of the ligands complexing the metal and several hydrido metal complexes are known in which the ligands are nitrogen, oxygen, sulfur or halogen donors, as for example $[RhH(NH_3)_5]^{2+}$ and $[CrH(H_2O)_5]^{2+}$.[31] They can be generated using various reactions, such as hydrolysis of $M(BH_4)_n$ complexes and by reaction of metal complexes ML_n with tetrahydroborate(III).[30]

The characteristics of hydrido metal complexes are, in addition to hydridic behaviour, protonic behaviour, depending on the metal and on the ligands:[32]
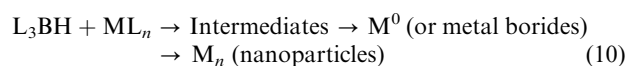
$$L_nM–H \rightarrow L_nM^- + H^+; \text{ acidic behaviour} \quad (7)$$

$$L_nM–H \rightarrow L_nM^+ + H^-; \text{ hydridic behaviour} \quad (8)$$
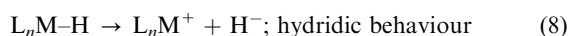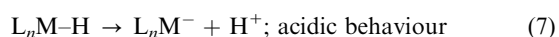
For example, $HCo(CO)_4$ and $HV(CO)_6$ are strong acids in water at 25 °C.[32]

Some neutral hydrido metal complexes can be protonated to form cationic hydrides, having characteristics similar to ammonia:[33]

$$L_2Re–H + H^+ \rightarrow L_2ReH_2^+ \ (L = C_5H_5) \quad (9a)$$

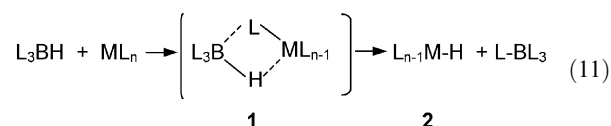$$L_2ReH_2^+ + OH^- \rightarrow L_2ReH + H_2O \quad (9b)$$

A general approach to a reaction scheme for CVG. In light of the above discussions, it appears reasonable that the reaction between tetrahydroborate(III) (or its hydroboron intermediates formed in the hydrolysis reactions (2)–(5)) and metal complexes takes place following the scheme:
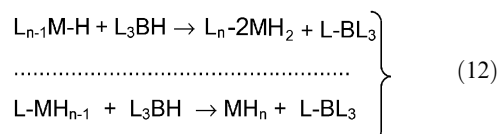
$$L_3BH + ML_n \rightarrow \text{Intermediates} \rightarrow M^0 \text{ (or metal borides)}$$
$$\rightarrow M_n \text{ (nanoparticles)} \quad (10)$$

In the case of a metal complex reacting with a borane complex $[L_3BH]^m$ (here L could also be H^-), it may be assumed that the

following reaction occurs:

$$L_3BH + ML_n \rightarrow \left[L_3B\underset{H}{\overset{L}{\diagdown}}ML_{n-1}\right] \rightarrow L_{n-1}M\text{-}H + L\text{-}BL_3 \quad (11)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

Further reactions of **2** with L_3BH result in formation of polyhydrides, up to the final reaction forming MH_n:

$$\left.\begin{array}{l} L_{n-1}M\text{-}H + L_3BH \rightarrow L_n\text{-}2MH_2 + L\text{-}BL_3 \\ \text{...} \\ L\text{-}MH_{n-1} + L_3BH \rightarrow MH_n + L\text{-}BL_3 \end{array}\right\} \quad (12)$$

The reaction scheme hypothesized above is of general validity. The reactivity is controlled by the coordination spheres of both the analyte and hydroboron species which, as noted, is related to the nature of both the metal M and the ligands, L. The stability of the intermediates plays a role in determining the reaction path, and therefore the nature of the final product. If all the intermediates containing one or more M–H bonds are stable, then the final product MH_n will be obtained, as in the case of the classical hydride forming elements. For example, further evolution of hydrido metal complex **2** could lead to formation of a binary hydride:

$$L_{n-1}M–H \rightarrow M–H + (n-1)L \quad (13)$$
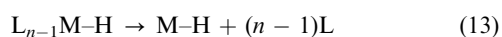
which further evolves according to the properties of hydride M–H, for example, yielding hydrogen due to hydridic behaviour:

$$M–H + H_2O \rightarrow M^0 + H_2 + OH^- \quad (14)$$

Hypotheses on the nature of the volatile species. Reaction (10) indicates the nature of possible volatile metal species. Free atoms and nanoparticles, the latter resulting from coalescence processes, have already been proposed as the "volatile" species.[34] Other hypotheses should include neutral molecular intermediates, such as those formed in reactions (11)–(13). For example, it is known that CuH is a solid that can be obtained by reaction of aqueous Cu(II) with hyphophosphite or $NaBH_4$[35] and gaseous AuH, AgH, CuH[36] and RhH[37] have been obtained by gas-phase reaction of hydrogen with laser ablated free atoms, together with many other compounds of the type MH_2, MH_3 and $(H_2)MH$ and $(H_2)MH_3$ (M = Cu, Ag, Au, Rh). A complex of molecular hydrogen with borane, $(H_2)BH_3$, has already been hypothesized as an intermediate in the hydrolysis of tetrahydroborate(III):[38]

$$BH_4^- + H^+ = H_3B\underset{H}{\overset{H}{\vert}} \rightarrow [BH_3] + H_2 \quad (15)$$
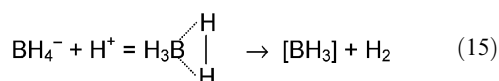
which is responsible for H/D exchange in tetrahydroborate(III) (see also refs. 20 and 39, p. 191). In conclusion, volatile metal species may also be transient, neutral molecular species of the type L_nMH_x, where L could be H_2O, OH^-, Cl^- or even H_2.

Some examples of the above concepts could be given by the reactivity of Hg(II) and Au(III) compounds. Following aqueous phase reaction with tetrahydroborate(III), Hg^{2+} gives rise to Hg^0. The HgH_2 hydride cannot be isolated, even if its existence has been recently demonstrated[40] in the solid state at temperatures below 150–170 K. In the case of $R–Hg^+$, alkyl and arylmercury compounds give RHgH (which could be classified as a particular case of a hydrido metal complex) possessing limited but significant stability at room temperature.[41] Recently, Xu and Sturgeon[42] reported that use of a mixed $NaBH_4$–$NaBEt_4$ reagent enhanced CVG efficiency 10-fold for production of volatile gold species compared to reaction with either $NaBH_4$ or $NaBEt_4$ alone. This could be due, by analogy with mercury, to the formation of hydrido metal complexes Et_nAuH_x

($n + x = 3$) having greater stability than that of the hydrides, $(H_2)_nAuH_x$ ($n = 0, 1; x = 1–3$) or other hydrido metal complexes L_nAuH_x (L = Cl$^-$, OH$^-$, etc).

Interactions of metal species with spray chamber surfaces. In general, two potential interactions with wetted surfaces exposed to the reaction solutions are possible:

(i) a fraction of the unreacted analyte, ML_n (L = H_2O, OH$^-$, Cl$^-$, etc.) is complexed by functional groups present on the reaction surface. In this case, new metal complexes, $Y_mL_{n-m}M$ (Y is functional group on the surface possessing donor/ligand properties) can be formed on the surface. For example, on a glass surface, silanol functional groups are present:

$$\text{-Si-O-}ML_{n-1} \qquad \begin{array}{c}\text{-Si-O}\\ \text{-Si-O}\end{array}ML_{n-2} \qquad \begin{array}{c}\text{-Si}\\ \text{-Si}\end{array}O \rightarrow ML_{n-1} \quad (16a)$$
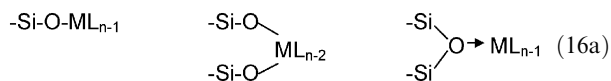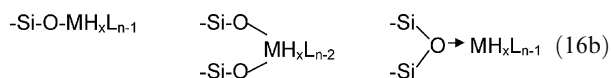
(ii) a reaction intermediate comprising the metal, L_nMH_x, becomes immobilized on the surface to yield different hydrido metal complexes, $Y_mL_{n-m}MH_x$:

$$\text{-Si-O-}MH_xL_{n-1} \qquad \begin{array}{c}\text{-Si-O}\\ \text{-Si-O}\end{array}MH_xL_{n-2} \qquad \begin{array}{c}\text{-Si}\\ \text{-Si}\end{array}O \rightarrow MH_xL_{n-1} \quad (16b)$$

With respect to metal ion complexes and hydrido metal complexes, it is reasonable to assume that the latter are more reactive towards the functional groups on the glass spray chamber surface. In the case of a Ryton surface, interactions of ML_n, or L_nMH_x should occur with ligands containing sulfur present in different functional groups (–C–SH, –C=S, –C–S–C–, etc.) on this material.

Part 2

Preliminary consideration of experimental results. Reactions of transition and noble elements with tetrahydroborate(III) were earlier categorized into four groups, based on criteria relating to memory effect, performance in glass *vs.* Ryton spray chambers, and the effect of the acid generation medium.[43] Thus, group 1 includes Cu, Pd, Ag, Au, Pt, Co, Ni, Rh and Tl, which suffer from memory effects with a glass spray chamber (no memory effects encountered with a Ryton system) and have a response nearly independent of the type of acid used as the generation medium but for which the Ryton surface provides significantly better sensitivity. Group 2 comprises Ti, Mn, Ir and Zn, which are free of memory effects, for which the Ryton surface provides significantly better sensitivity and for which generation appears to be essentially independent of the type of acid used. Group 3 includes Cd, In, Hg and Pb, which suffer no memory effects but performance is superior (by typically five-fold) when the species are generated in a glass spray chamber. Additionally, response is somewhat sensitive to the type of acid used in the generation medium. Finally, group 4 comprises As, Se and Sb, which suffer no memory effects, enhanced performance when generated in a glass system and whose response is independent of the type of acid used in the generation medium.

The focus of this study has been the group 1 elements. Within this group the electron configuration for Ag, Au, Pt, Pd and Cu (denoted Ag subgroup) has a full "d" or "f" electron shell (d^{10}, f^{14}) whereas Rh, Co and Ni have an unfilled "d" shell configuration (denoted Rh subgroup). Thus, group 1 is further divided into two sub-groups, based on their electron configuration and, for this reason, are discussed separately below.

Silver subgroup. The response from gold in the Ryton system passes through a maximum with increasing concentration of hydrochloric acid, but this does not occur in a nitric acid medium. A possible explanation may be that reactions (11) and

(12), being strongly influenced by the nature of the ligands, are sensitive to matrix composition. In nitric acid media the most common ligand species for Au(III) are H_2O and OH$^-$, while in dilute hydrochloric media the dominant species is $AuCl_3(OH)^-$ or $AuCl_{4-n}OH_n^-$, depending on experimental conditions.[44] Excessive chloride concentrations limit the generation efficiency by suppressing the extent of the reaction, suggesting that $AuCl_4^-$ is not a good precursor for the formation of volatile species. The presence of some hydroxide ligand group therefore appears to promote the formation of the volatile Au species.

Further information is provided by the influence of the spray chamber material on memory effects. Gold suffers a serious memory effect when using a glass spray chamber[43] but this does not occur in a Ryton system. Fig. 1 presents a typical signal arising from the generation of Au in a system fitted with either a glass or Ryton spray chamber. With a glass spray chamber fitted with a 12.5 cm inner Ryton tube, the integrated response is about 30% of that obtained when an inner glass tube of the same dimensions is used (Table 1). This implies that 70% more of the gold introduced into the system remains immobilized on the glass surface of the inner tube from which it is subsequently volatilized after a second interaction with blank–NaBH$_4$ reaction mixture. It is possible that the immobilized species are unreacted $AuCl_{4-n}(OH)_n^-$ complexes, but it is difficult to imagine a spray chamber material exhibiting such high memory effect towards aqueous complexes of metal ions. Such a memory effect could be due to very active species of gold being formed during reaction with NaBH$_4$, most probably hydrido metal complexes, L_nAuH_x. Thus, for the glass spray chamber, wherein the aqueous phase uniformly wets the surface, interactions with silanol groups may occur according to Scheme 16b and give rise to a serious memory effect (*cf.* Au trace in Fig. 1). The newly formed gold complexes on the surface are then able to generate volatile species in a secondary reaction with hydroboron species.

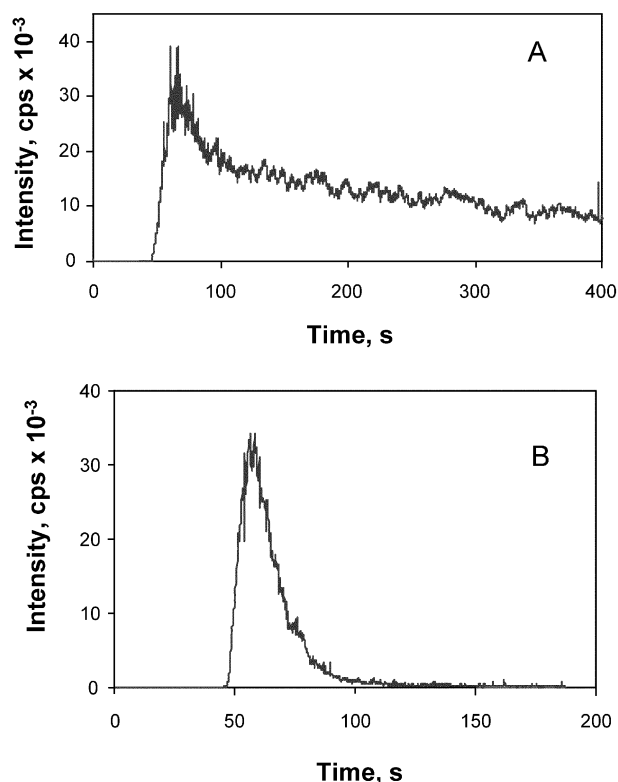

Fig. 1 Typical response from Au with FIA sampling. Injection loop is 0.08 ml; [Au] = 200 ng ml^{-1}; [HCl] = 0.5 M; [NaBH$_4$] = 1% (m/v) in 0.001 M NaOH solution. A: *glass* double-pass spray chamber, B: *Ryton* double-pass spray chamber.

Table 1 Effect of spray chamber inner tube length and material on response[a]

	Ryton spray chamber			Glass spray chamber		
	G–12.5[b]	G–4.5[b]	R–12.5[b]	R–12.5[b]	G–12.5[b]	Optimum acidity (M)
^{65}Cu	3700[c] [(52)] [d]	2500[(28)]	4500[(200)]	2650[(120)]	6100[(70)]	HCl (0.25)
^{106}Pd	3900[(60)]	2800[(30)]	5700[(220)]	3500[(150)]	11460[(170)]	HNO$_3$ (0.5)
^{107}Ag	14 300[(700)]	9800[(180)]	25 600[(1700)]	19 100[(1200)]	19 700[(500)]	HNO$_3$ (0.5)
^{195}Pt	430[(9)]	350[(4)]	650[(40)]	480[(24)]	890[(16)]	HCl (0.5)
^{197}Au	11 700[(180)]	9400[(170)]	5100[(180)]	10 100[(190)]	34 900[(150)]	HNO$_3$ (1)
^{59}Co	4000[(80)]	2700[(60)]	7500[(280)]	2400[(80)]	1750[(20)]	HCl (0.1)
^{60}Ni	850[(37)]	810[(31)]	1500[(87)]	810[(43)]	1900[(22)]	HNO$_3$(0.05)
^{103}Rh	6600[(130)]	6600[(90)]	8900[(450)]	5200[(280)]	14 500[(140)]	HCl (0.5)
^{55}Mn	110[(8)]	110[(4)]	780[(41)]	560[(28)]	250[(9)]	HCl (0.1)
^{114}Cd	15 730[(570)]	6700[(250)]	1000[(54)]	1240[(80)]	18 200[(700)]	HCl (0.1)
^{121}Sb	238 000[(11 000)]	250 000[(12 000)]	156 000[(8000)]	220 000[(9300)]	361 000[(15 000)]	HCl (0.5)

[a] 0.08 ml injection loop; R: Ryton; G: Glass. [b] Inner length of tube (cm). [c] Integrated response, counts ppb^{-1}. [d] Peak height response, counts s^{-1} ppb^{-1}. Typical RSD is 10–15% for replicate signals.

With a Ryton spray chamber, intermediates formed during the reduction reaction either interact with and are immobilized by sulfur functional groups on this surface, as was the case for Cd and Hg,[24] or they do not react at all and are rapidly removed from the system because of efficient physical drainage imparted by the hydrophobic Ryton surface. Consequently, a sharp signal peak is obtained when using the Ryton system (compare peak intensity data in Table 1).

It is reported that Au(I) complexes of the type (R$_2$S)Au–X (X$^-$ = halogen, pseudohalogen, RS$^-$, *etc.*) are useful intermediates for synthetic purposes.[44] The positive effect of micro amounts of DDTC on the CVG of volatile gold species following the reaction of Au(III) with aqueous NaBH$_4$ is in line with the above mentioned chemical properties.[19] As such, a reasonable hypothesis could be the reduction of the Au(III) complex to an Au(I) complex and finally to Au(0), where the intermediate specie, X$_n$AuH$_x$, can be chemisorbed onto a glass surface by interaction with free silanol groups, but subsequently released by slow reaction with BH$_4^-$ or its hydrolysis products (hydroboron species, H$_2$). In the case of a Ryton surface, it may be assumed that there is an inefficient chemisorption effect or that any chemisorbed species react quickly with hydroboron species.

Effect of inner tube. The effect of the material and the length of the inner (first pass) tube within the demountable Ryton spray chamber on signal shape and intensity was examined. Glass tubes of constant internal diameter but increasing length were utilized to explore the different characteristics of the silver group elements and conventional hydride-forming elements. Results in Table 1 clearly demonstrate that the mechanism of vapor generation for transition and noble metals (groups 1, 2 and 3) follows different routes from those of conventional hydride-forming elements (group 4). For brevity, only data for Mn(II), Cd(II) and Sb(III) are presented as representative elements of groups 2, 3 and 4, respectively. With the longer inner tube present in the double-pass Ryton system, higher peak intensities for transition and noble metals occur than in a similarly fitted double-pass glass system. However, the Ryton system gives lower peak intensities than the glass system for conventional hydride-forming elements. When the outer shell of the spray chamber consists of Ryton and the inner tube is glass, the shape of the signal for silver improves as the inner tube length decreases. This is consistent with the shorter interaction time between intermediates and the glass surface (reactions (16a) and (16b)). As the length of the glass tube is reduced, less silver is chemisorbed on the surface. In the case of continuous flow experiments, the generation efficiency obtained using a glass system is superior to that obtained with

Ryton because the analyte is continuously chemisorbed and "time" accumulated on the surface (the signal generated by continuous flow introduction tends to slowly increase with time).

When a Ryton inner tube is fitted to an exterior glass chamber, the signal shape and intensity for silver improves and the background is substantially reduced. This implies the occurrence of a secondary reaction within the inner tube of the spray chamber. When the system is completely glass, the signal shape does not change but the peak intensity increases with decreasing inner tube length. As noted above, this is consistent with decreased efficiency of the secondary reaction when interaction times with the reactive glass surface are enhanced. Although peak intensities are greater in the Ryton system than in the glass system, the integrated response is higher in the latter, which implies that the analyte remains as a reactive intermediate on the spray chamber surface and continues to react with hydroboron species in the acidic environment relatively long after the initial mixing of the solutions. The long tail on the Au signal, evident in Fig. 1, further supports the suggestion that the secondary reaction is maintained for an extended period of time on a glass surface.

By contrast, vapor generation is rapidly terminated in the Ryton system, as evidenced by the data in Table 2 which show that the analyte concentrations in the waste solution draining

Table 2 Estimated generation efficiencies

	Generation efficiency[a] (%)		
	Ryton	Glass	Silanized glass
^{65}Cu	30	48	28
^{106}Pd	74	69	25
^{107}Ag	60	73	24
^{195}Pt	74	65	25
^{197}Au	62	72	24
^{59}Co	58	75	8
^{60}Ni	62	40	10
^{103}Rh	80	82	58
^{55}Mn	86	78	49
^{114}Cd	83	90	18
^{121}Sb	98	100	96

[a] Continuous sample introduction system; results based on calculation of the relative loss of analyte from the feed solution, [1 − (C_w/C_0)] × 100, where C_w and C_0 are analyte concentrations in waste and in feed and solutions, respectively, averaged over a 2 min collection interval. Typical RSD is 10–15% for all data.

from the spray chamber are typically higher than those in the glass system. It is noteworthy that if the glass surface is first silanized, the concentration of analyte in the waste solution is substantially elevated, a clear indication of the active role played by both Ryton and glass systems in improving the production of volatile species through secondary reactions promoted by the wetted surface. In the case of silanized glass, secondary reactions are strongly inhibited and the volatile species are those arising only from the primary reactions, *i.e.*, homogeneous phase reactions in the aqueous solution between ML_n and hydroboron species. Compared to the conventional hydride-forming elements, the vapour generation efficiency is substantially lower for the silver group elements.

If a nylon mesh (mesh dimensions 0.2 mm) is inserted into the inner tube of either spray chamber, such that it covers the entire portion of its interior surface, the signal intensity is uniformly reduced, as evidenced by the data in Table 3 for the Ryton and glass systems. This likely arises because the mesh inhibits efficient drainage of the solutions and supports a substantially increased film thickness (approximating a bulk solution) which may retard immediate escape of the volatile species to the gas phase, leading to their enhanced decomposition. Furthermore, because the mesh appears to equalize the response from both spray chambers, this increased water film thickness must also influence the generation process. Note that conventional hydride-forming elements are not affected by either the presence of these surfactants nor the mesh on the inner tube surface as they are characterized by formation of stable intermediates/products, which are amenable to efficient transport from the bulk solution. The signal intensity can be somewhat recovered in a Ryton system fitted with a mesh insert (about 2–4 fold the intensity obtained with the mesh present) if Triton X-100[TM] or antifoam-B is also present in the sample solution. By contrast, addition of these reagents is not sufficient to recover the response in a glass system fitted with a mesh but, in fact, further decreases response.

Rhodium subgroup. Fig. 2 presents a typical signal for Rh generated in a system fitted with either a glass or a Ryton spray chamber. A serious memory effect occurs with the glass spray chamber. In contrast to silver, however, response from Rh is sensitive to the concentration of both nitric and hydrochloric acids, rather than simply to the presence of chloride ions, as evident in Fig. 3. If the inner surface of the glass tube in a glass spray chamber is rinsed by introduction of various solutions immediately after introducing the acidic sample and tetrahydroborate(III) reagent, some interesting observations arise, as summarized in Table 4. Cessation of the sample and reductant should result in immediate quenching of the signal and, if memory effects arise as a result of a simple release process, the Rh signal should still be observed during rinsing with water. However, during rinsing with water no Rh signal is obtained. However, following rinsing periods ranging from 2 to 20 min, resumption of introduction of an acid blank (0.5 M HCl) and reductant solution results in the reappearance of a Rh signal, which persists for a relatively long period of time (more than 40 min). This suggests the presence of a Rh species chemisorbed onto the surface. This may be unreacted Rh(III) retained by

Table 3 Effect of surfactants and nylon mesh on response using a double-pass Ryton or glass spray chamber

Ryton spray chamber

	A	B	C	D	E	F
^{65}Cu	4500^a$_{(200)}$^{b}	7800$_{(450)}$	11 000$_{(450)}$	560$_{(24)}$	2000$_{(120)}$	1600$_{(100)}$
^{106}Pd	5800$_{(240)}$	9200$_{(150)}$	14 000$_{(180)}$	600$_{(40)}$	2700$_{(140)}$	2300$_{(110)}$
^{107}Ag	25 600$_{(1710)}$	13 000$_{(780)}$	17 000$_{(900)}$	2400$_{(130)}$	4700$_{(300)}$	4277$_{(220)}$
^{195}Pt	650$_{(40)}$	60$_{(4)}$	160$_{(7)}$	50$_{(2)}$	23$_{(1)}$	31$_{(2)}$
^{197}Au	5200$_{(180)}$	11 000$_{(130)}$	11 000$_{(130)}$	400$_{(20)}$	1800$_{(90)}$	1700$_{(80)}$
^{59}Co	7300$_{(280)}$	1500$_{(40.5)}$	2700$_{(70)}$	500$_{(8)}$	300$_{(10)}$	540$_{(20)}$
^{60}Ni	1400$_{(90)}$	500$_{(10)}$	700$_{(5)}$	250$_{(5)}$	170$_{(3)}$	260$_{(6)}$
^{103}Rh	8907$_{(450)}$	6200$_{(340)}$	23 000$_{(900)}$	2700$_{(90)}$	2100$_{(140)}$	2400$_{(140)}$
^{55}Mn	780$_{(40)}$	450$_{(20)}$	410$_{(20)}$	150$_{(7)}$	100$_{(5)}$	140$_{(8)}$
^{114}Cd	1100$_{(60)}$	3400$_{(160)}$	4600$_{(210)}$	4300$_{(230)}$	6500$_{(250)}$	7700$_{(370)}$
^{121}Sb	157 000$_{(8500)}$	176 000$_{(9400)}$	240 000$_{(14\,000)}$	250 000$_{(13\,000)}$	160 000$_{(7800)}$	190 000$_{(14\,000)}$

Glass spray chamber

	A	B	C	D	E	F
^{65}Cu	6116^a$_{(69.5)}$^{b}	5057$_{(214)}$	12826$_{(300)}$	945$_{(13.8)}$	2966$_{(180)}$	2461$_{(140)}$
^{106}Pd	11 460$_{(170)}$	4358$_{(95)}$	7985$_{(117)}$	780$_{(16)}$	2437$_{(66.7)}$	2384$_{(65.1)}$
^{107}Ag	19 700$_{(490)}$	10 542$_{(501)}$	25 245$_{(700)}$	1693$_{(80)}$	5940$_{(350)}$	5874$_{(342)}$
^{195}Pt	886$_{(15.6)}$	97$_{(3.7)}$	695$_{(5)}$	38.8$_{(1.6)}$	49.3$_{(2.8)}$	40.4$_{(2)}$
^{197}Au	23 760$_{(202)}$	17 550$_{(231)}$	32 870$_{(275)}$	1940$_{(47)}$	9390$_{(157)}$	8250$_{(146)}$
^{59}Co	1736$_{(19.8)}$	1929$_{(13.3)}$	18 327$_{(123)}$	279$_{(6.7)}$	488$_{(12.5)}$	799$_{(17.5)}$
^{60}Ni	1935$_{(23.4)}$	1867$_{(21.9)}$	25 390$_{(173)}$	391$_{(7.7)}$	556$_{(11.4)}$	821$_{(16.8)}$
^{103}Rh	14 558$_{(136)}$	5560$_{(204)}$	24 738$_{(422)}$	1799$_{(70)}$	2587$_{(136)}$	3792$_{(225)}$
^{55}Mn	248$_{(9.1)}$	160$_{(9.1)}$	321$_{(16.2)}$	131$_{(7)}$	145$_{(8.0)}$	166$_{(7.9)}$
^{114}Cd	18 350$_{(727)}$	18 470$_{(730)}$	18 210$_{(728)}$	17 335$_{(653)}$	16 940$_{(617)}$	13 080$_{(498)}$
^{121}Sb	361 750$_{(15\,600)}$	315 360$_{(14\,380)}$	300 700$_{(14\,130)}$	287 500$_{(12\,960)}$	308 750$_{(11\,540)}$	239 530$_{(9530)}$

Conditions: 0.08 ml injection loop. A: Sample without Triton X-100[TM]. B: Sample and carrier containing 0.002% Triton X-100[TM]. C: Sample and carrier containing 0.005% Triton X-100[TM], tetrahydroborate(III) reductant contains 0.01% antifoam agent. D: Nylon mesh covering inner surface of first pass tube, no Triton X-100[TM]. E: Nylon mesh covering inner surface of first pass tube, sample and carrier containing 0.002% Triton X-100[TM]. F: Nylon mesh covering inner surface of first pass tube, sample and carrier containing 0.005% Triton X-100[TM], tetrahydroborate(III) reductant contains 0.01% antifoam agent. ^{a} Integrated response (counts ppb^{-1}). ^{b} Peak height response (counts s^{-1} ppb^{-1}) given in parentheses. Typical RSD is 10–15% for replicate signals.
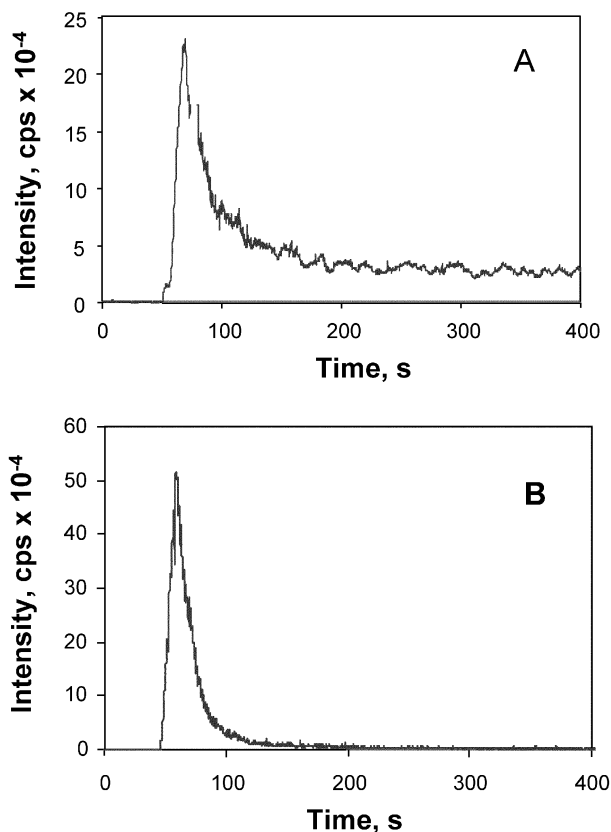
Fig. 2 Typical response from Rh with FIA sampling. Injection loop is 0.08 ml; [Rh] = 100 ng ml^{-1}; [HCl] = 0.5 M; [NaBH$_4$] = 1% (m/v) in 0.001 M NaOH solution: (A) *glass* double-pass spray chamber, (B) *Ryton* double-pass spray chamber.

silanol groups. It is noteworthy that [Rh(H$_2$O)$_6$]$^{3+}$ behaves as an acid in aqueous media,[44] *i.e.*:

$$[Rh(H_2O)_6]^{3+} + H_2O \rightarrow [Rh(H_2O)_5(OH)]^{2+} + H_3O^+;$$
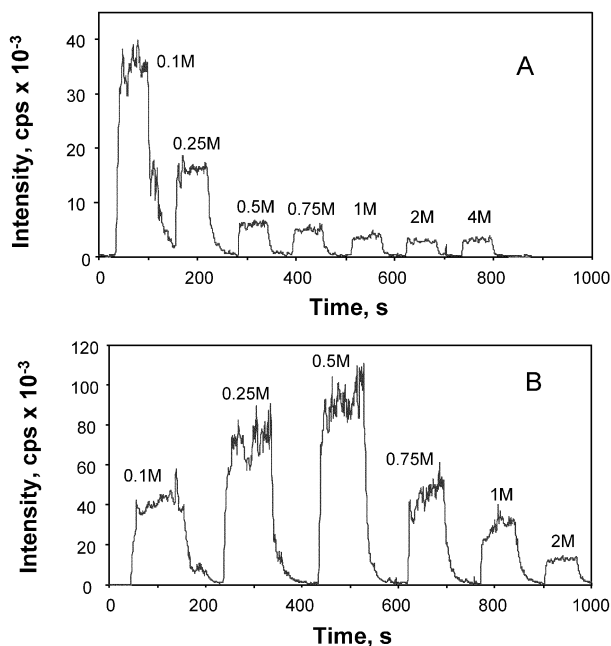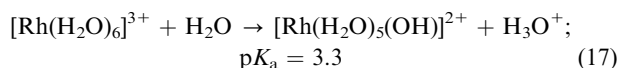$$pK_a = 3.3 \qquad (17)$$

Fig. 3 Effect of acid concentration on generation of Rh using a *Ryton* double-pass spray chamber: [Rh] = 100 ng ml^{-1}; [NaBH$_4$] = 1% (m/v) in 0.001 M NaOH solution: (A) nitric acid, (B) hydrochloric acid.

Table 4 Effect of drying the spray chamber with Ar or air on washout intensities

Rinse reagent	Memory effects[a]
H$_2$O	Rapid rise and decay of peak, rinsed out using water before returning to blank intensity
NH$_4$Ac (5%)	Rapid rise and decay of peak, easily rinsed out using water before returning to blank intensity
NaOH (0.5 M)	Very slow decay, rinsed out using water before returning to blank intensity
HAc (5%)	Very slow decay, only partially rinsed out using water before returning to blank intensity
HCl (0.5 M)	Very slow decay, only partially rinsed out using water before returning to blank intensity
HNO$_3$ (0.5 M)	Slow decay, only partially rinsed out using water before returning to blank intensity
H$_2$O$_2$ (3%)	No decay, signal can not be rinsed out using water

The peak intensity for the blank and the rate of decay of the signal (washout time) increased with increased drying time. Argon accomplishes the same function as air, implying that the high peak blank and signal decay is a response to drying and not to a chemical reaction with oxygen or nitrogen. Drying is necessary and important; if no drying process is permitted, the volatile compounds cannot be released and a high peak is subsequently obtained on introduction of a blank solution. Rh was prepared in 0.5 M HCl and the blank is 0.5 M HCl. Air and argon gas flow rate used for drying was 0.55 l min^{-1}. Drying time was approximately 10 min. [a] Response following introduction of a 100 ppb solution of Rh.

In hydrochloric acid media [Rh(H$_2$O)$_n$Cl$_{6-n}$]$^{(3-n)}$ (n = 0–3) should be formed, for which no particular acid–base behaviour is reported.[44] Based on the above argument, it seems unlikely that unreacted Rh(III) species are responsible for this effect. A second observation supporting this hypothesis is that, as in the case of gold, for a glass spray chamber fitted with a 12.5 cm inner Ryton tube the integrated signal is about 35% of that obtained when using a glass spray chamber fitted with a 12.5 cm inner glass tube (Table 1). This suggests that 65% of the rhodium being introduced is immobilized on the glass surface from which it is volatilized in a second interaction with a blank NaBH$_4$ reaction mixture. For the same reason proposed for gold, such a marked memory effect is likely due to a very active species of rhodium being formed during reaction with NaBH$_4$, most probably hydrido metal complexes, L$_n$–Rh–H$_x$.

Several experiments were conducted wherein the inner surface of the glass tube of the spray chamber was rinsed with various solutions (0.5 M HCl, water, 0.5 M NH$_4$Ac or 0.5 M NaOH) for 2 min and then dried in a stream of Ar before being wetted again by introducing water for 1 min. Following this, hydrochloric acid (0.5 M) blank and tetrahydroborate(III) reductant were then introduced. If rinsing was performed with a neutral or basic solution, the drying procedure efficiently removed all Rh complexes adsorbed to the surface of the inner glass tube, thereby completely eliminating the Rh memory effect. However, if an acidic solution was used as the rinse agent, the Rh complex(es) remained on the surface of the inner glass tube, irrespective of whether an intermediate drying procedure was implemented or not (*cf.* Table 4). If a drying procedure is undertaken and a rinse of the inner surface of the inner glass tube with water is not performed before introducing the blank and reductant solutions, a large Rh signal occurs. It appears that the chemisorbed Rh species reacts with OH$^-$ but not with H$^+$ to generate a new species which is easily removed by water or is capable of being converted to a volatile species after a drying step. This may be explained by assuming the formation of hydrido rhodium intermediates [L$_n$RhH$_x$]$^+$, formed according to reactions (11) and (12), which present
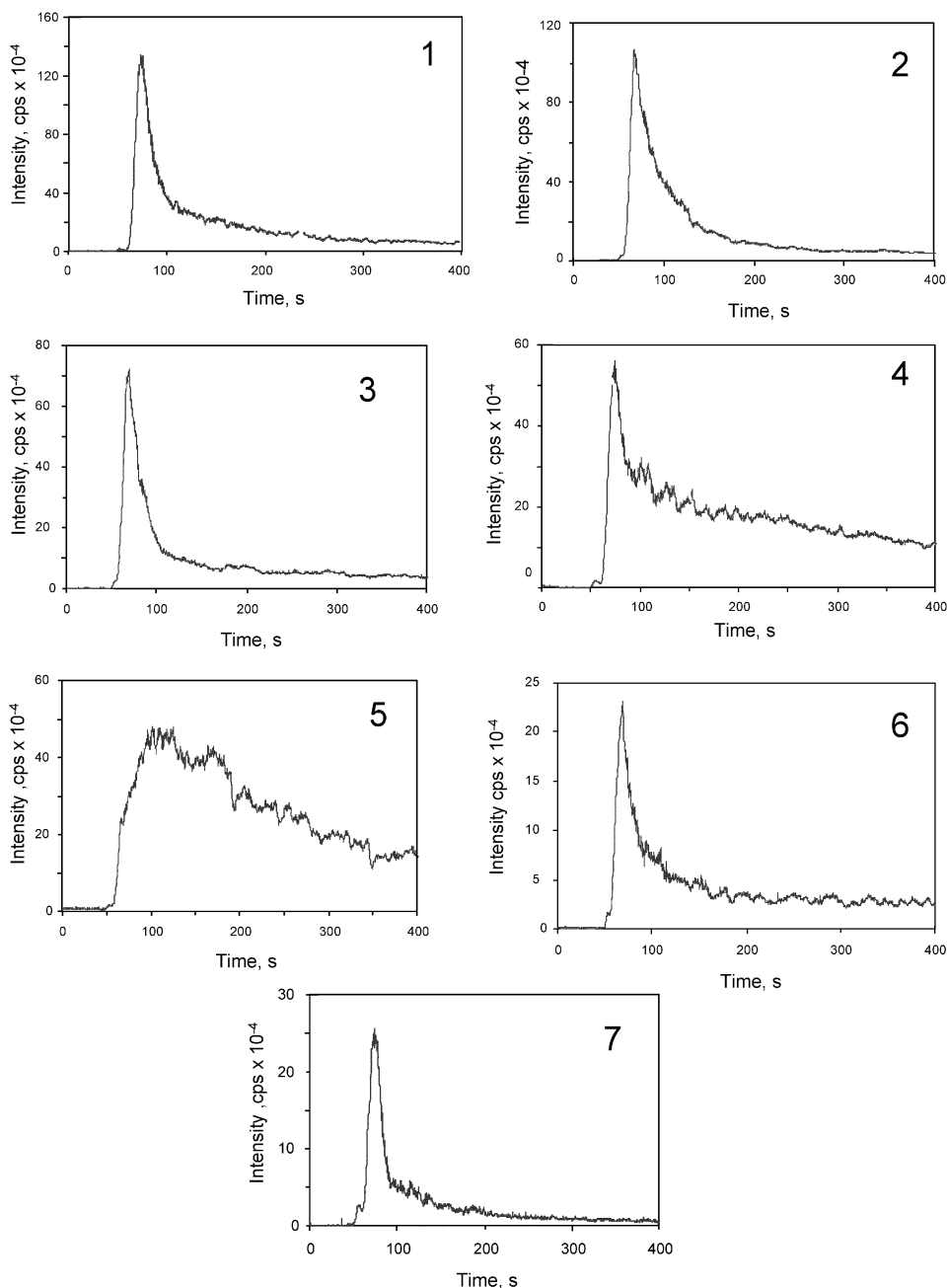
Fig. 4 Interaction between intermediates of Rh vapor generation and Triton X-100^{TM} and antifoam agent B in a glass spray chamber system. Injection loop is 0.08 ml; [Rh] = 100 ng ml^{-1}; [NaBH$_4$] = 1% (m/v) in 0.001 M NaOH. The NaBH$_4$ solution was introduced continuously during the entire measurement. (1) 30 s introduction of 0.5 M HCl containing 0.013% antifoam agent B followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM}. (2) 30 s introduction of 0.5 M HCl containing 0.013% of antifoam agent B followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl. (3) 30 s introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM} followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl. (4) 30 s introduction of 0.5 M HCl containing 0.02% Triton X-100^{TM} followed by injection 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.013% antifoam agent B. (5) 30 s introduction of 0.5 M HCl followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.013% antifoam agent B. (6) 30 s introduction of 0.5 M HCl followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl. (7) 30 s introduction of 0.5 M HCl followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% Triton X-100^{TM}.

an acid/base behaviour similar to that reported in reactions (9a) and (9b), *i.e.*:

$$[L_nRhH_x]^+ + OH^- \rightarrow L_nRhH_{x-1} + H_2O \qquad (18)$$

$$[L_nRhH_x]^+ + L_3BH \rightarrow L_nRhH_{x-1} + L_3B + H_2 \qquad (19)$$

$$[L_nRhH_x]^+ + L_3BH \rightarrow L_nRhH_{x+1} + L_3B \qquad (20)$$

Data in Table 3 (Ryton and glass systems) show that a mesh placed on the inner surface of the interior Ryton or glass tube

reduces the Rh signal intensity. This may occur for either of two reasons: (i) the CVG efficiency is unaffected but the volatile Rh species cannot be released to the gas phase because it is unstable and decomposes or is trapped in the thicker water film provided by the mesh; (ii) CVG of Rh requires a surface to support the reaction because it is not a direct one step process. In the first step, the Rh(III) is reduced to an intermediate species (eqns. (10)–(12)) that readily interacts with functional groups on the glass surface (reactions (16a) and (16b)), whereupon it is (chemi)sorbed. This intermediate continues to react with BH$_4^-$
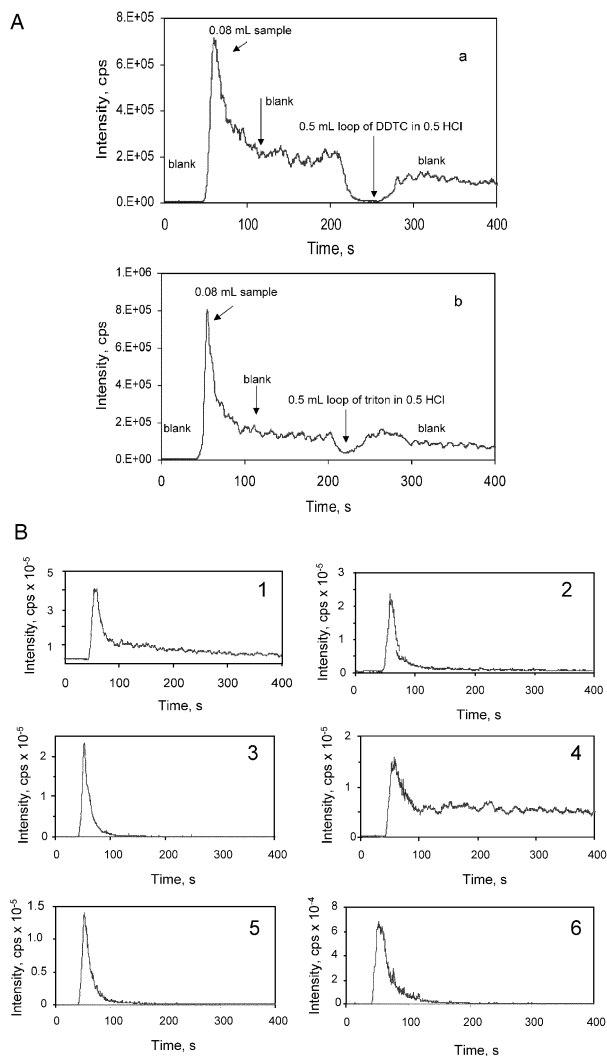
Fig. 5 (A) Interaction of the Rh intermediate produced during vapor generation with complexing agents in a glass spray chamber. (a) 30 s introduction of 0.5 M HCl followed by injection of a 0.08 ml loop of 100 ng ml^{-1} Rh(III) in 0.5 M HCl containing 0.02% Triton X-100^{TM}; at 3 min, injection of a 0.5 ml loop of 0.02% DDTC in 0.5 M HCl. Blank is 0.5 M HCl. NaBH$_4$ solution [1% (m/v) in 0.001 M NaOH containing 0.013% antifoam agent B] was introduced continuously during the entire measurement time period. (b) 30 s introduction of 0.5 M HCl followed by injection of a 0.08 ml loop of 100 ng ml^{-1} Rh(III) in 0.5 M HCl containing 0.02% of Triton X-100; at 3 min, injection of a 0.5 ml loop of 0.02% Triton X-100^{TM} in 0.5 M HCl. Blank is 0.5 M HCl. NaBH$_4$ solution (1% (m/v) in 0.001 M NaOH containing 0.013% antifoam agent B) was introduced continuously during the entire measurement time period. (B) Interaction of the Rh intermediate produced during vapor generation with complexing agents and surfaces within the glass spray chamber. (1) Inner glass tube (first pass) of spray chamber with no nylon mesh present. 30 s introduction of 0.5 M HCl containing 0.02% Triton X-100^{TM} followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% Triton X-100^{TM}. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH and 0.013% antifoam B] was introduced continuously during the entire measurement time period. (2) Inner glass tube of spray chamber with no nylon mesh present. 30 s introduction of 0.5 M HCl with 0.02% of Triton X-100^{TM} inside followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM}. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH] was introduced continuously during the entire measurement time period. (3) Nylon mesh covering inner surface of glass tube of spray chamber. 30 s introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM} followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM}. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH and 0.013% antifoam B] was introduced continuously during the entire measurement time period. (4) Inner glass tube of spray chamber with no nylon mesh present. 30 s introduction of 0.5 M HCl followed by injection of 0.08 ml of 100 ng

and its hydrolysis products (L$_{4-n}$BH$_n$, H$_2$) to subsequently generate the volatile Rh species. These processes give rise to the Rh memory effect in the glass system. The data in Table 3 (Ryton and glass systems) show that Triton X-100^{TM} and antifoam-B agent are useful for recovering the Rh signal in the presence of the mesh and increasing the Rh signal intensity in a system without the mesh. Triton X-100^{TM} is a non-ionic surfactant and antifoam-B agent consists of a mixture of non-ionic detergents which may interact with the Rh intermediates during vapor generation or serve to reduce film thickness by decreasing the solution surface tension, thereby promoting release to the gas phase. Several other complexing agents (diethyldithiocarbamate, didodecyldimethylammonium bromide, and sodium ethylenediaminetetraacedic acid) were examined in an effort to determine if there was any effect on Rh response, but changes were insignificant compared with those arising from the presence of the surfactants. The role of the surfactant and antifoam agents is thus not yet completely clear.

The presence of the mesh within the inner glass tube eliminates the memory effect for Rh in this system. As noted above, evidence suggests that memory effects in the glass system arise as a result of an interaction between an intermediate species and the glass surface and if this interaction can be prevented, the memory effect disappears. Fig. 4 illustrates both the enhancement effects of Triton X-100^{TM} on the Rh signal intensity and its suppression of memory effects in a system fitted with a glass spray chamber. On the other hand, the antifoam B agent enhances both the signal intensity and the memory effects in a system fitted with a glass spray chamber. If attention is focused on the memory stage, injection of a loop containing Triton X-100^{TM} or other reagent (*e.g.*, 0.02% DDTC) completely suppresses the Rh memory effect when continuously introducing 0.5 M HCl along with tetrahydroborate(III) reductant containing antifoam B agent. This is illustrated in Fig. 5 and again suggests that intermediate species are present on the glass surface and that use of complexing agents prevents surface adsorption. Recall the loss of signal when a silanized glass surface was used—this also suggests that prevention of the secondary reaction from occurring in the generation sequence has been achieved.

Remarks on observed surface effects. Concerning group 1 elements, both glass and Ryton surfaces appear to play a role in the formation of volatile metal species. Indeed, when the surface is chemically inert, as in the case of silanized glass (see Table 2), a general decrease in response is observed for all metals. Therefore, the following summary of the observed behaviour can be made:

(a) silanized spray chamber—the volatile species are those formed in homogeneous phase reactions, the *primary reaction*. They arise during the period of time starting from the mixing step in the nebulizer until the impact of the reaction mixture with a surface. No further reactions would take place on the

ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH] was introduced continuously during the entire measurement time period. (5) Nylon mesh covering inner surface of glass tube of spray chamber. 30 s introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM} followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl containing 0.02% of Triton X-100^{TM}. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH] was introduced continuously during the entire measurement time period. (6) Nylon mesh covering inner surface of glass tube of spray chamber. 30 s introduction of 0.5 M HCl followed by injection of 0.08 ml of 100 ng ml^{-1} Rh in 0.5 M HCl, followed by continuous introduction of 0.5 M HCl. The NaBH$_4$ solution [1% (m/v) containing 0.001 M NaOH] was introduced continuously during the entire measurement time period.

surface (chemisorption, *secondary reactions* of chemisorbed species with hydroboron species), except the eventual further mixing of reagent and sample solution, which represents the completion of the *primary* reaction.

(b) glass spray chamber—in addition to the volatile species formed during the *primary* reaction, more volatile species are formed by surface mediated reactions (*secondary* reactions). Indeed, metal species can be efficiently chemisorbed on the surface by reactions such as (16a) or (16b). The newly formed complexes on the surface may then react with hydroboron species at different rates. Slow rates of the *secondary* reaction introduce a delay between the primary and secondary reactions which is responsible for signal tailing (memory effect) and, in general, controls the signal shape in a glass spray chamber.

(c) Ryton spray chamber—in addition to the volatile species formed during the *primary* reaction, additional volatile species are formed in a *secondary* reaction arising from species chemisorbed onto the Ryton surface by reactions similar to those represented by (16a) or (16b), but involving sulfur as the donor group. No signal tailing is observed, indicating that this *secondary* reaction is much faster than the corresponding one taking place on the glass surface.

Conclusions

The mechanism of vapor generation of transition and noble metals is apparently more complex than the one for conventional hydride-forming elements.
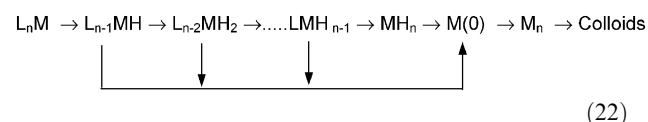
This apparently different behaviour is probably due to the different paths followed by the analyte intermediate during the reaction with tetrahydroborate(III) or its hydrolysis products.

In the case of the classical hydride forming elements, the analyte species (L_nM) are progressively converted to the final stable hydride through the stepwise replacement of L groups by hydrogen (reactions (11) and (12)):

$$L_nM \rightarrow L_{n-1}MH \rightarrow L_{n-2}MH_2 \rightarrow \ldots LMH_{n-1} \rightarrow MH_n \quad (21)$$
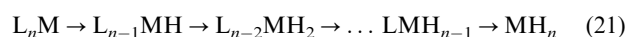
wherein all the intermediate and final hydrides are stable species.

In the case of transition and noble metals, the final product stability is often very low, while the stability of the intermediates is strictly related to the nature of the ligand species. Whereas many stable hydrido metal complexes (L_nMH_x) have been synthesized with high field ligands (CO, phosphines, cyclopentadienyl...*etc*.), unstable hydrido metal complexes are typically obtained in the case of low field ligands (H_2O, OH^-, halogen ions, *etc*.). Nevertheless, their lifetime could be long enough to drive a process which results in the formation of the volatile metal species (most likely neutral) observed in many recent CVG studies. The possibility of detecting volatile species is dramatically related to the rate of the liquid-gas phase transfer step. If this step is not fast enough, only the final stable products will be observed, which sequentially include: free atoms, metal nanoparticles, colloids and macro precipitates:

$$L_nM \rightarrow L_{n-1}MH \rightarrow L_{n-2}MH_2 \rightarrow \ldots LMH_{n-1} \rightarrow MH_n \rightarrow M(0) \rightarrow M_n \rightarrow Colloids \quad (22)$$

The effects produced by different surface materials encompassing the reaction system provide evidence for the existence of reaction intermediates which can efficiently produce volatile metal species through surface mediated reactions with $NaBH_4$ or its hydrolysis products. The initially proposed two step mechanism[24] can therefore be expanded into a more general multi-step mechanism, assuming the existence of intermediates between aqueous complexes of the analyte, L_nM, and the reduced metal, M(0).

The identity of the volatile species transported and detected during CVG remains to be determined and this presents a serious obstacle to full comprehension of the mechanistic details of the CVG of transition and noble metals. However, the many different chemical properties of hydrido metal complexes, in addition to those of free atoms and nanoparticles, serve as a basis for explanations of such complex results observed during CVG as the memory effects, the acid–base behaviour observed during rinsing experiments, the effect of added surfactant and other additives as well as many other observations noted in the present and previous studies.[1–19,43]

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