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Surfactant assisted chemical vapour generation of silver for AAS and ICP-OES: a mechanistic study†

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A chemical vapour generation (CVG) procedure for the production of volatile species of Ag was developed and studied using AAS and ICP-OES detection. A characteristic mass of 0.12 ng was achieved using a miniature diffusion flame atomizer-AAS system, whereas a 38-fold higher sensitivity (as cps per ng of introduced analyte) compared with conventional liquid nebulization was obtained with ICP-OES. The overall efficiency of introduction of Ag to the plasma was verified to be over 20%. More than one order of magnitude enhancement of efficiency was obtained by the addition of a surfactant (Triton X-100 in combination with an antifoaming agent), the effect of which, however, cannot be ascribed to the formation of organized media. Experiments concerning the mechanism of the CVG, transport and memory effect are discussed: Ag CVG is not a simple one-step process as is the case for CVG of selenium, but rather a two-step procedure. Transport properties of the volatile Ag species resemble more the transport of the liquid aerosol than a simple gaseous species such as H₂Se. Possible alternatives concerning the identity of the volatile metal species are presented.

Introduction

The undisputable advantages associated with conversion of the analyte to a volatile form and its separation from the matrix as an introduction technique for analytical spectroscopy, well established in the case of the generation of volatile hydrides,¹ have recently led to a quest for expansion of the technique to noble and transition metals.^{2–14} The production of volatile species (chemical vapour generation, CVG) of Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rh, Pd, Ag, Ir, Au and Pt (in addition to Hg and Cd) by the reduction of metal ions by tetrahydroborate(III) has been described, and analytical procedures for the determination of Cu,² Zn,³ Au⁴ and Ag, Au, Co, Cu and Ni⁵ have been published.

Despite this, very little is known about the nature and mechanism of production of such species. In contrast to Hg and Cd, molecular species are certainly produced, as free atoms were not observed without an “atomization” environment.^{3,4,6} Metal hydrides are usually cautiously suspected,^{2,3,6,7} but never proven beyond doubt.

The aim of this study was to obtain a deeper insight into the processes leading to the production of volatile metal species, as well as their identity. The possibility of chemical modification of the CVG process by surfactants^{15,16} was also explored. Silver was chosen as the model element and the experimental setup is based on an earlier AAS study.⁸ Initial tests were performed using AAS with a diffusion flame atomizer to avoid possible volatile species transport problems, as this setup avoids any transfer line.⁸ Afterwards, the ICP-OES was selected as the technique of choice because its multielement capability allowed simultaneous detection of any volatile metal species, hydride forming elements and aerosol transported fractions arising from the sample.

Experimental

AAS instrumentation

An AAAnalyst 100 atomic absorption spectrometer (Perkin-Elmer Corp., Norwalk, CT, USA) was used, fitted with a Ag

hollow cathode lamp (SCP Science, Baie D'Urfe, QC, Canada) operated at 10 mA. The resonance line of 328.1 nm was monitored using a spectral bandpass of 0.7 nm. No background correction was used and repeat readings were taken using an integration time of 15 s. Steady-state sample introduction was examined.

ICP-OES instrumentation

An IRIS axial plasma ICP-OES spectrometer (Thermo Jarrell Ash Corp., Franklin, MA, USA) with echelle grating polychromator and CID detector was used (with the exception of the determination of Ag in waste liquid—see below). The operating conditions are summarized in Table 1. The following lines were always simultaneously monitored: Ag 328.068 nm (in 79th order) and 338.289 nm (77); Mg 279.553 nm (93), 280.270 nm (93) and 285.213 nm (91); Se 196.090 nm (132) and 203.985 nm (127); Na 330.237 nm (79) and 330.298 nm (79). For the sake of brevity only data for the former line for each element are generally presented. For liquid sample nebulization, the IRIS multipass glass spray chamber fitted with Teflon insert and cross-flow nebulizer was used. Three replicate integration times of 30 s with read delay of 50 s and 240 s for solution nebulization and CVG, respectively, were used for measuring steady-state signals. Blank and standard solution measurement was always alternated. For the study of wash-out times, measurements were made using a 27 s integration time (total time 45 s per measurement) repeated continuously. Error bars in the figures represent ± 1 standard deviation.

Table 1 IRIS spectrometer operating conditions

RF power	1150 W
Plasma gas flow rate	15 l min ⁻¹
Sample nebulization using cross-flow nebulizer:	
Intermediate (auxiliary) gas flow rate	0.5 l min ⁻¹
Nebulizer gas pressure/flow rate	22 psi/300 ml min ⁻¹
Sample uptake flow rate	1.85 ml min ⁻¹
CVG sample introduction:	
Intermediate (auxiliary) gas flow rate	1 l min ⁻¹
Make-up gas flow rate	350 ml min ⁻¹
CVG carrier gas flow rate	150 ml min ⁻¹
Sample and reductant flow rates	0.4 ml min ⁻¹

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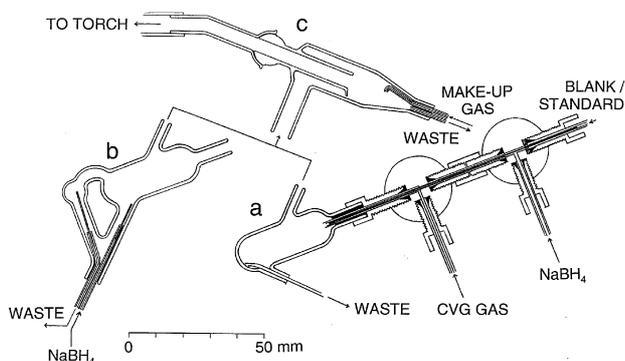


Fig. 1 a, CVG system; b, hydrostatic GLS with additional NaBH_4 channel; c, CVG-ICP-OES interface/spray chamber.

CVG system

The continuous flow CVG system is based on the arrangement described earlier,⁸ and is depicted in Fig. 1a. The core of this system consists of three concentric capillaries: the two inner ones (id 0.25 mm and 0.53 mm) are made of deactivated fused silica tubing and used for the introduction of sample/standard and reductant solutions, respectively; the outermost one (id 1 mm) is made of PTFE and served to introduce a purge gas (CVG gas). The ends of the capillaries all terminated 1 mm apart, see ref. 8 for an expanded diagram of the capillary junctions. The three concentric capillaries enter the glass gas-liquid separator (GLS), the same as is used on the commercial hydride generation system (PerkinElmer FIAS 200, Bodenseewerk PerkinElmer, Germany). For some experiments, hydrostatic GLS (Fig. 1b) was used, wherein a stable liquid level is maintained and allows the addition of another NaBH_4 flow into the pool of liquid inside the GLS. The system was mounted so that its axis was sloping at a 22.5° angle. All connections were made using $1/4''$ -28 flangeless fittings and polyether ether ketone (PEEK) T-pieces. Blank/standard and reductant solutions were introduced by a peristaltic pump (Gilson Minipuls II, Villiers le Bel, France) or the spectrometer built-in pump fitted with 0.76 mm id Tygon tubes. The same, or a separate, identical pump was also used for removal of the waste solution from the GLS, using 2.29 mm id Tygon tubing. A small degassing chamber, made of Teflon (volume approximately 0.5 ml) was included in the reductant line.⁸

For AAS experiments, a miniature diffusion flame atomizer consisting simply of a 12 mm long quartz capillary (1.8 mm id, 3.5 mm od)⁸ was connected directly to the outlet of the gas-liquid separator. The CVG system-atomizer replaced the burner, so that the radiation beam passed directly over the top of the atomizer. Argon and hydrogen, both at flow rates of 45 ml min^{-1} , were used as the carrier gas for this atomizer, which were the lowest flow rates capable of supporting a stable diffusion flame.

The CVG connection to the plasma torch required a special interface to permit the addition of a make-up gas, as it also served as a spray chamber, and was mounted at a right angle to the CVG system. The connection was sealed on the GLS outlet by Teflon tape with one layer of filter paper in the seal, or by a short piece of Tygon tubing (experiments with trapping on filter).

Reagents

All working solutions were prepared in a Class 100 environment using $18 \text{ M}\Omega \text{ cm}$ (NanoPure, Model D4744, Barnstead/ThermoLine, Dubuque, IA, USA) deionized water (DIW). High-purity sub-boiling-distilled HNO_3 prepared in-house from reagent grade feedstock was used for preparation of standards and blanks. Mixed standard solutions were prepared by serial

dilution from 1000 mg l^{-1} of individual element stock solutions (Ag^I , Mg^{II} , Se^{IV}) in 1 M HNO_3 . Triton X-100 (Aldrich Chemical Co., Milwaukee, WI, USA) was added to the standards using 0.2% (m/v) in DIW stock solution prepared from the reagent.

Reductant solutions (all figures in % (m/v)) were prepared daily from NaBH_4 caplets (Alfa Aesar, Ward Hill, MA, USA) and stabilized by 0.1% (m/v) NaOH (Anachemia, Montreal, QC, Canada). Antifoam B (AFB, BDH Inc., Toronto, ON, Canada), a water-dilutable 10% active silicone emulsion designed to control foam in aqueous systems, was added as 1:10 (v/v) stock solution prepared from the reagent. The reductant solution was paper filtered (for the AAS experiments only). It was found that the filtration caused high Mg blanks and thus was omitted for ICP-OES work.

Compressed Ar and H_2 were obtained from Air Products Canada Ltd. (Nepean, ON, Canada).

Procedures

Trapped and residual Ag determination

The determination of Ag in various compartments following the CVG process was performed. A $0.3 \text{ M HNO}_3 + 20 \text{ mg l}^{-1}$ Triton X-100 solution was used throughout for blank and standard preparation: $1.2 \text{ NaBH}_4 + 1 : 7500 \text{ AFB}$ in 0.1% NaOH served as reductant. The volatilized Ag was trapped on 25 mm diameter, $0.45 \mu\text{m}$ pore size syringe filters (Cole-Parmer Instrument Co., Cat. No. P-02915-22) attached to either the GLS outlet or the spray chamber outlet.

With the unconditioned system (*i.e.*, trapping performed during the first introduction of Ag into a cleaned system), the CVG system was thoroughly cleaned first using 6 M HNO_3 . The CVG process was started by generation from 5 ml of blank solution. Then, without stopping the pump, the filter was attached and CVG from a 10 ml solution of 1 mg l^{-1} Ag and 1 mg l^{-1} Mg, followed by 5 ml of blank, was performed. The waste liquid was collected and the GLS was rinsed for retained Ag determination, as described below.

With the conditioned system, the CVG system was thoroughly cleaned first using 6 M HNO_3 and then CVG of 6 blank/standard cycles (5 ml each) was performed and signal intensity data recorded. The CVG was then disconnected from the plasma torch and, without stopping the pump, a filter was attached and CVG from a 10 ml solution of 1 mg l^{-1} Ag and 1 mg l^{-1} Mg, followed by 5 ml of blank, was performed and the waste liquid collected.

The Ag retained on the filters was recovered by slowly passing 5 ml of hot 6 M HNO_3 through them by use of a syringe (over a 2 min period) followed by 5 ml of DIW and the eluent diluted to 25 ml in a volumetric flask. The GLS and the waste tubing were leached by gradually filling them with 5 ml of hot 6 M HNO_3 followed by 5 ml of DIW and diluting the rinse to 25 ml in a volumetric flask. The waste liquid was added to 10 ml of 6 M HNO_3 and diluted with DIW to 50 ml in a volumetric flask; 25 ml of this solution were spiked with $50 \mu\text{l}$ of a 50 mg l^{-1} solution of Ag and $50 \mu\text{l}$ of a 50 mg l^{-1} solution of Mg.

The Ag content in the individual fractions was determined using the Optima 3000 ICP-OES (PerkinElmer Corp., Norwalk, CT, USA) fitted with a cross-flow nebulizer and double-pass Scott-type spray chamber. The Ag and Mg content in the filters and the GLS fractions were determined using external calibration. Such contents in the waste liquid were determined using the method of standard additions.

Results and discussion

CVG optimization-AAS experiments

The CVG system described earlier⁸ was further developed, with special attention devoted to the possibility of the use of

chemical modification by surfactants. Preliminary testing and optimization of the CVG parameters was performed using the simple diffusion flame atomizer and AAS detector. Initially, a peak area characteristic mass of 15 ng was achieved; this may be compared to a value of 7 ng published earlier⁸ under identical concentrations and pump flow rates (1 M HNO₃ and 1% NaBH₄ at 0.6 ml min⁻¹). The slightly higher carrier gas flow rates that were necessary to maintain the diffusion flame may, however, contribute to the difference.

The influence of the addition of the non-ionic surfactant (Triton X-100) to the sample solution was tested, and the results depicted in Fig. 2. Clearly, a 4-fold increase in the sensitivity (in fact, CVG efficiency, as the atomization parameters were not altered) is observed with a sharp maximum at 20 mg l⁻¹ of X-100 in the sample solution, followed by a decrease at higher concentrations. However, this enhancement cannot be explained by enhancement of CVG from an organized medium,^{15,16} because the optimum surfactant concentration in the reaction mixture (1.7 × 10⁻⁵ M) is more than one order of magnitude lower than the critical micelle concentration (CMC) of X-100 (2.2–2.4 × 10⁻⁴ M¹⁷). The possible mechanism of action of the surfactant will be discussed in more detail below; 20 mg l⁻¹ of X-100 was thus used throughout in further work. No other surfactants were tested.

A similar enhancement effect due to the presence of surfactant (cetyltrimethylammonium bromide, CTAB) was reported on the determination of Zn³⁺ at a CTAB concentration well under the CMC (2.5 × 10⁻⁵; CMC_{CTAB} = 0.9 × 10⁻³), which was (erroneously) ascribed to the effect of an organized medium.

Reductant concentration was optimized in the presence of surfactant in the range of 0.5–4% NaBH₄. A 3% NaBH₄ solution was found to be optimum, with signal approximately 4-fold higher than that obtained using 1% NaBH₄.

In order to decrease foam formation in the GLS, an antifoaming agent (Antifoam B) was added to the reductant solution, as has been reported in some studies with organized media.^{18,19} This resulted in up to a 2.5-fold increase in the signal intensity compared to the system without AFB. However, after stopping the AFB addition, the Ag sensitivity immediately decreased by only about 20%, clearly exhibiting a strong memory effect. Various dilutions of the AFB were tested: the 1:10000 dilution was too low to achieve maximum signal intensity, but 1:5000 dilution, on the other hand, caused a slow gradual decrease in the Ag signal. A dilution of 1:7500 was found optimal and used throughout further work. Apparently, the AFB does not simply act by physically suppressing foam formation, but also plays a role in other processes, as discussed below.

The linearity of the response was checked: the influence of the sample flow rate was measured (reductant flow rate was

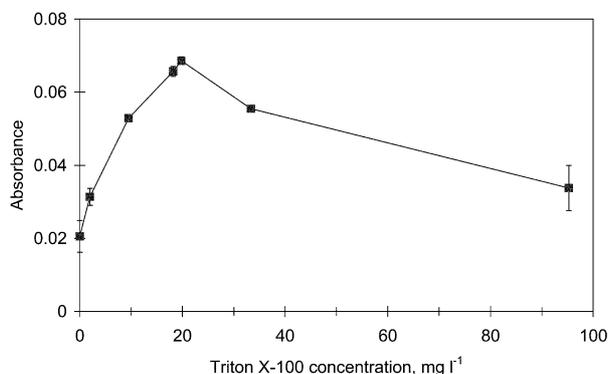


Fig. 2 Influence of Triton X-100 concentration in the sample on the CVG-AAS Ag absorbance. (5 mg l⁻¹ Ag in 1 M HNO₃; 1% NaBH₄ at 0.6 ml min⁻¹).

increased proportionally in this case). Results are presented in Fig. 3 in comparison to the calibration graph at constant sample flow rate (0.6 ml min⁻¹). When the sample flow rate increased beyond 0.5 ml min⁻¹, the signal no longer increased linearly and, in fact, a decrease was observed at a flow rate of 1 ml min⁻¹. A nonlinear increase of the signal with sample flow rate was earlier reported;^{7–9} however, the explanation may be difficult due to the complexity of the processes, the difference in the reductant and waste flow rates, as well as the effect of the amount of liquid remaining in the GLS (see below). A flow rate of 0.4 ml min⁻¹ was chosen for further work to ensure the highest possible efficiency of production of volatile Ag species.

After this preliminary optimization and application of the surfactant/antifoaming agent for chemical modification, a characteristic mass of 0.12 ng was achieved for Ag. This is a remarkable improvement, considering the value of 7 ng reported earlier using a similar arrangement,⁸ and the 1.7 ng obtained using classical nebulization–flame atomization with the same AAS instrument. A 4% RSD precision (at 0.5 mg l⁻¹) was achieved with the CVG procedure. No attempts were made to determine the actual limit of detection for this procedure, as the diffusion flame has a very short length for the absorbing layer. To obtain superior limits of detection, a heated quartz tube atomizer⁸ or multiple microflame quartz tube atomizer²⁰ for AAS should be employed.

ICP-OES experiments

CVG–plasma torch interface setup. The coupling of the CVG system to the plasma torch necessitated two basic requirements: supply the make-up gas required for optimum plasma conditions, and reject aerosol droplets containing high concentrations of sodium produced in the CVG generator.

This was attempted first using a simple T-piece connection to a multipass spray chamber. However, this connection suffered from liquid condensation in the T-piece and tubing before reaching the actual spray chamber, finally resulting in an extensive build-up of salts in this tubing. Substitution of the multipass spray chamber for a cyclonic one did not influence the signal, indicating that the actual droplet size discrimination is performed in the tubing and/or T-piece prior to the spray chamber. Other attempts at connecting the CVG without the T-piece (by using an 80 mm length of 1/8" tubing) and introducing the make-up gas at various points inside the cyclonic spray chamber by inserting tubing through the waste outlet, did not solve the problem of droplet formation in the connecting tubing and yielded much worse sensitivity and/or precision.

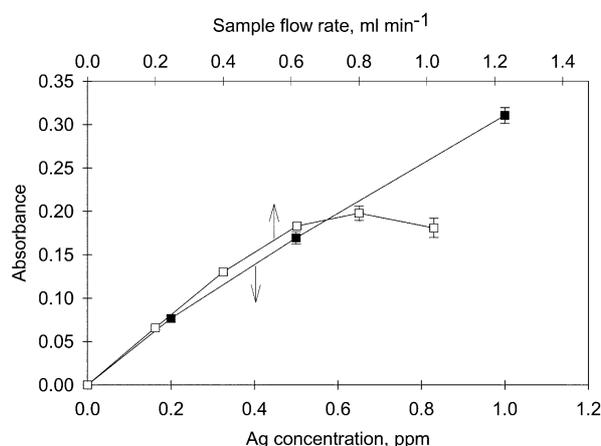


Fig. 3 Influence of the Ag supply rate on CVG-AAS absorbance. ■, Ag calibration graph (sample flow rate 0.6 ml min⁻¹); □, Ag supply at various sample flow rates (0.5 mg l⁻¹ Ag). Standards prepared in 1 M HNO₃ + 20 mg l⁻¹ Triton X-100; reductant 3% NaBH₄ + AFB 1:7500. Reductant flow rate the same as sample flow rate; waste removal flow rate increased proportionately.

The use of a cyclonic spray chamber as the functioning GLS was also not successful—the Ag signal decreased by 97%, even if almost no Mg and Na signals were detected (Se signal decreased by only 10%); the likely reason for this was probably the poor conditions for transport of Ag volatile species (whose transport properties apparently differ from properties of SeH_2 , see below) out of the GLS.

The problem of large aerosol droplets was finally solved by the use of a miniature double-pass spray chamber (see Fig. 1c), which permitted long term use due to continuous removal of the condensing liquid from both the connecting line and the spray chamber itself, without degradation of sensitivity. Liquid is removed by a layer of filter paper in the GLS–spray chamber connection seal (not shown) as liquid soaks through the paper and dries on the exterior surface and is also pumped out of the spray chamber.

Several positions for the introduction of make-up gas were tested (spray chamber interior, beginning and end of the outlet tube, at both its axis and close to its wall). The most sensitive and reproducible results were achieved if the tip of the introduction capillary was located either close to the wall of the spray chamber outlet tube, or in its interior close to the wall (see Fig. 1c: the capillary tip was tilted so that gas flows in around the wall in cyclonic fashion). As most of the aerosol was deposited around the point of introduction of the make-up gas, the latter arrangement was chosen for further work because it is easier to remove droplets from the spray chamber interior than from the outlet tube.

The dried aerosol formed solid white deposits inside the spray chamber. Saturation of the make-up gas with water vapour (by bubbling it through a water column) appeared to alleviate this problem since under these conditions the deposited droplets did not dry up, but rather flowed down to where they could be pumped to waste. With this arrangement, the system could be operated continuously without the need for cleaning or drying.

Fig. 4 shows the effect of make-up gas and CVG gas flow rates on normalized ICP-OES response for Ag. Obviously, CVG gas flow rates under 150 ml min^{-1} are not sufficient for the efficient transport of Ag species, whereas at a higher flow rate more aerosol is transported into the plasma (the total gas flow rate entering the plasma was kept constant at 550 ml min^{-1} to maintain constant plasma conditions). A flow rate of 150 ml min^{-1} of Ar as the CVG gas was used in further work.

The make-up gas must be added to achieve optimum plasma operating conditions. Results of optimization of total gas flow rate to the plasma (including constant CVG gas flow rate of 150 ml min^{-1}) are also depicted in Fig. 4. The Ag signal is constant in the range $400\text{--}500 \text{ ml min}^{-1}$, whereas the signals

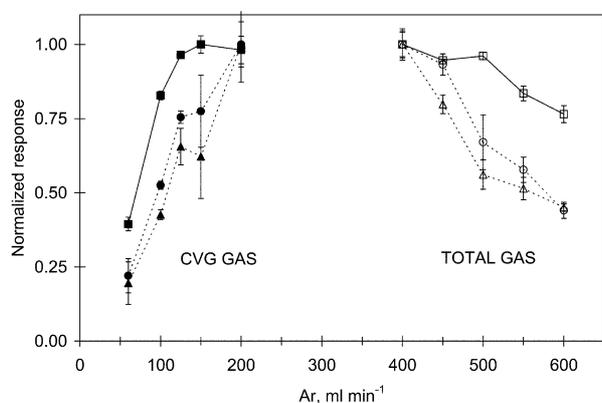


Fig. 4 Influence of CVG and total gas flow rate on sensitivity. CVG gas: total gas flow rate 550 ml min^{-1} ; total gas flow rate includes CVG gas 150 ml min^{-1} . ■, □: Ag; ●, ○: Mg; ▲, △: Na.

for elements expected to be associated with aerosol (Mg, Na) decrease with increasing flow rate. This is probably due to more efficient removal of aerosol as a result of more pronounced turbulent forces; a much lower decrease is experienced for Ag and Se (not shown) intensities and the Mg 280.2:Mg 285.2 line ratio remains constant. However, a change in sensitivity due to changes in plasma conditions cannot be excluded. A make-up gas flow rate of 350 ml min^{-1} was used in further work, yielding a total gas flow rate to the plasma of 500 ml min^{-1} .

CVG parameters

Waste removal rate. A strong influence of the liquid level in the GLS, or the waste liquid removal rate, on the signal intensity was noted, similar to that reported in ref. 9. A small pool of liquid is necessary for efficient CVG, whereas aerosol production increases only slowly. On the other hand, a higher level of liquid slightly decreases the signal as well as aerosol formation. Moreover, the waste liquid should not be removed from the liquid surface because it causes signal instability, as observed earlier.⁸ Liquid was therefore removed close to the bottom and the liquid level was controlled by careful setting of pump speed. The effect of the waste removal pump rate on signal for two sets of acid– NaBH_4 concentrations is shown in Fig. 5. The optimum volume of liquid needed in the GLS is approximately 0.25 ml. A comparison of signals with and without this pool of waste liquid at the bottom of the GLS (*i.e.*, at optimum and highest waste pump rate in Fig. 5) suggests that, in fact, only 25–30% of the Ag transported to the plasma is released before the liquid enters the pool. Most probably, even this is accomplished from the droplets retained on the GLS walls.

On the contrary, Se release is completed at this step (although another 20% of Se can be volatilized from the pool of waste liquid by introducing an additional flow of reductant). Moreover, aerosol carryover is increased by only 10–20% in the presence of the pool. This suggests that Se hydride release, as well as aerosol formation, is accomplished prior to or upon the impact of the liquid on the walls. This is confirmed by additional experiments wherein stopping sample/reductant flows to the capillary was undertaken, as described below.

$\text{HNO}_3\text{--NaBH}_4$ concentrations. Obviously, in a complex system such as CVG, which includes chemical as well as physical processes, the optimum acid and reductant concentrations are not independent of each other. Therefore, a biparametric optimization was performed with respect to Ag sensitivity and aerosol production. The resulting response surface is depicted in Fig. 6. Conditions characterized by a slight surplus of H^+ are needed—the residual pH of the reaction mixture is slightly acidic (at pH values higher than necessary for efficient selenium hydride generation, which is

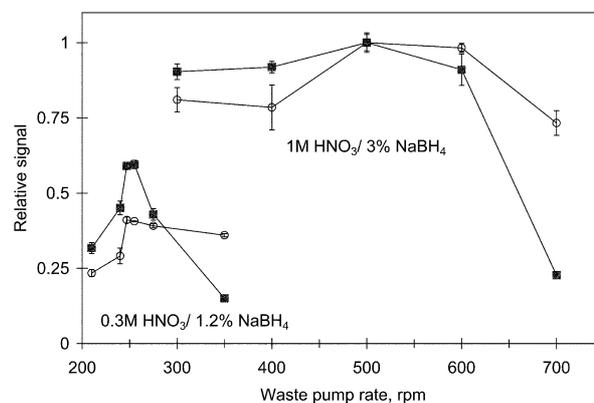


Fig. 5 Effect of waste removal pump rate on normalized ICP-OES response for two sets of $\text{HNO}_3\text{--NaBH}_4$ concentrations: ■, Ag; ○, Mg.

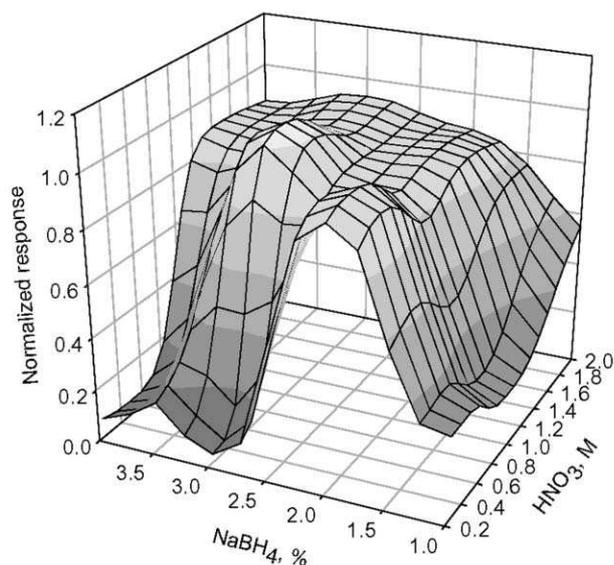


Fig. 6 Response surface for biparametric optimization of HNO_3 and NaBH_4 concentrations. Ag 328.068 nm line; waste removal pump rate 400 rpm.

reduced to about 30% of optimum under these conditions), whereas it is strongly reduced under conditions of excess NaBH_4 . A slower decrease is observed at higher acidities. Aerosol carry-over, monitored using the Mg signal, shows similar trends to the Ag signal; the Na signal decreases proportionally to the NaBH_4 concentration. Unfortunately, these results are biased by the different level of waste liquid in the GLS at a constant waste removal pump rate: at higher reductant concentrations, more hydrogen (which has high volume compared to the liquid) is produced in the waste pump tube as a result of decomposition of residual NaBH_4 and removal of waste liquid is less efficient. At low reductant concentrations, there is, in fact, no waste liquid remaining in the GLS, which is reflected in the low response shown in Fig. 6. The biparametric optimization with fast removal of waste liquid (not shown) yielded similar trends and optimum conditions at reduced sensitivity, with the exception of the signal decrease at the lowest reductant concentrations. Therefore, an optimum HNO_3 concentration was determined, with the residual liquid level carefully maintained. For a NaBH_4 concentration of 1%, 0.25 M HNO_3 was found to be optimum. The resulting sensitivity for Ag was 66% compared with the most sensitive combination (0.6 M HNO_3 –2.4% NaBH_4), whereas 67% and 23% of Mg and Na signal, respectively, were obtained. Solutions of 0.3 M HNO_3 –1.2% NaBH_4 were chosen for further ICP-OES work, as sodium carryover to the plasma is greatly reduced compared to 1 M HNO_3 –3% NaBH_4 solutions which were found optimum in the AAS study.

CVG sensitivity compared with liquid nebulization

A comparison of sensitivities for CVG and liquid nebulization of Ag, Se (hydride forming element) and Mg (aerosol element) is summarized in Table 2. The efficiency of introduction of Ag

Table 2 Comparison of ICP-OES sensitivities for liquid nebulization and CVG sample introduction

Line	CVG sensitivity/ cps ng^{-1}	Nebulization sensitivity/ cps ng^{-1}	Enhancement factor
Ag 328.068 nm	540	14	38
Se 196.090 nm	12.6	0.073	173
Mg 279.553 nm	22.5	144	0.16

by CVG is about 38-fold greater than conventional nebulization (taking the sample solution flow rates into account), and roughly 4.5-fold worse than Se hydride generation efficiency by the same system. This is in general agreement with the conclusions arising from experiments on trapping Ag on in-line filters described below (assuming about 0.5% nebulization efficiency at 1.9 ml min^{-1} sample uptake, in accordance with Se data). Of course, different plasma conditions for CVG and liquid nebulization can influence these conclusions.

Sensitivity drift and memory effects

Visually, a blackish film is formed in the CVG system on the introduction capillary, starting at the point of sample–reductant mixing, and also over the GLS walls. “Greasy” deposits can also be observed in the spray chamber after prolonged use: they cannot be eliminated with HNO_3 , but can be removed with hexane; these are most probably the remnants of the antifoaming agent.

Sensitivity stabilization. After cleaning the CVG system with 6 M HNO_3 , it took at least 5 sample/blank cycles to achieve stable sensitivity with Ag, compared with only 1–2 cycles for selenium. The sensitivity obtained in the first cycle may be even less than 50% of the stable signal. This was shortened to about 3 cycles if the system was not thoroughly cleaned, with response in the first cycle starting at around 60–70% of the stabilized signal. The signal for the aerosol derived elements changes to a similar extent. Transport processes in the spray chamber (where small droplets on the surface are gradually formed) are probably the source of signal drift for aerosol derived elements, but probably not for Ag, as much less silver was retained on the filter in the unconditioned CVG system than under stabilized conditions (see below). The source of the signal drifts are the reactions within the liquid pool, which give rise to about 2/3 of the volatile Ag (sensitivity without the pool of liquid is reduced to around 30%).

If the removal rate of the waste liquid is fast (no liquid pool in the GLS), less than 10% sensitivity drift is observed, even with the cleaned CVG system, which can probably be ascribed to stabilization of the transport processes. As noted below, short wash-out times were obtained under these conditions.

Wash-out time. Signal wash-out times were tested under standard operating parameters with the pool of liquid in the GLS. The wash-out time for Ag (*i.e.*, time taken for the signal to decrease to 5% of its steady-state value) was 3.5 min. With a fast rate of removal of waste liquid (no liquid pool is present), the wash-out time decreased to 2 min. However, the sensitivity also decreased to about 25–35% of its former value. This clearly indicates that the pool of liquid in the GLS is the source of the long wash-out times, rather than deposits of Ag on the capillary tip and/or the walls of the GLS.

With the hydrostatic GLS (Fig. 1b), very long wash-out times were experienced for Ag—approximately 10 min. This may be caused by the waste being removed at a point far from the actual liquid level from which Ag species may possibly be volatilized and/or by increased possibilities for Ag to be deposited on the walls, as well as by the increase in the volume of remaining liquid from 0.25 to 0.5 ml.

By comparison, wash-out times were less than 1.5 min for both Mg (under all conditions) and Se (under optimum chemical conditions). Higher wash-out times were noted for Se at low acidity (the Se response was reduced to 25–30% compared with optimum values) wherein 2.5, 5 and 1.5 min resulted for standard, no pool and hydrostatic GLS conditions.

In an attempt to reduce the wash-out times and increase sensitivity, an additional flow of NaBH_4 solution (for identical concentration and flow rate, the acidity of the sample was increased to 0.6 M to assure NaBH_4 decomposition) was

introduced *via* a capillary to a point either 5 mm or 2 mm under the level of the liquid pool and 2 mm over the liquid in the hydrostatic GLS. However, no significant improvement in sensitivity, nor reduction in wash-out time, was observed for Ag. No change was noted for intensities for the aerosol elements Na and Mg. The Se signal intensity was increased by about 20%, with wash-out times remaining under 1.5 min.

An attempt to generate Ag species by introducing the reductant directly into the GLS liquid pool only produced a signal about 5% of optimum (whereas 30% of Se signal, 60% of Mg and almost no Na signal were observed). Most probably, this means that the NaBH₄ reaction near the liquid level does not produce conditions favorable for the release of species from the solution, possibly because extensive mixing disturbs the formation of the Ag enriched layer close to the liquid surface.

If the flow of the reductant or sample solution was stopped, the signal intensity immediately dropped to baseline. Thus, the long wash-out times are not just due to slow reaction and/or slow release of the volatile Ag species. A continuous supply of fresh reactants is necessary to react with the precursor or to promote release of the volatile species from the solution.

If the liquid in the GLS is quickly pumped out during the wash-out period, the signal decreases to the blank level; however, it returns to the level corresponding to the wash-out time after the fast liquid removal has been stopped and a stable liquid level restored. This suggests that the hypothetical volatile Ag species precursor is not present in the liquid, but rather adsorbed to the wall of the GLS, which is wetted by the liquid pool. If the liquid is quickly removed during the measurement, this precursor is either not deposited, or cannot be converted into the volatile form, producing a short wash-out time.

Suggested mechanism

The production of volatile Ag species most probably proceeds in two steps. The first step, formation of the volatile species or, more likely, their precursor, may correspond to the reduction of Ag⁺ to Ag⁰. This is a rather fast process, as a black precipitate is observed on the CVG capillary tips immediately at the point of sample/reductant mixing.

It is important to note that the optimum sensitivity for Ag is achieved at acid concentrations corresponding to an H⁺-NaBH₄ molar ratio of one or slightly higher. Slightly higher H⁺-NaBH₄ molar ratios were found optimum for Ag by Feng *et al.*, 3.8,¹⁰ and Duan *et al.*, 1.7-3.7.⁵ In comparison, according to published data, the optimum H⁺-NaBH₄ ratio for volatilization of noble metals (Au, Pt, Pd) is between 6 and 15,^{9,10} for Cu values of 1.7-3.7,⁵ 7.6¹⁰ or higher than 2.7 (HNO₃) or 6.7 (HCl)² have been used and for Ir, around 1.¹⁰ For Ni, Co and Zn an excess of reductant over H⁺ is generally required.^{5,7,10,11} These results may be explained by the different ability of the hypothetical volatile species precursor, supposedly reduced metal, to be re-dissolved by acids. However, this is not the case for Ir, which is practically insoluble in acids at room temperature. As well, a comparison of signal intensities arising from Cu and Ag in HCl and HNO₃ media^{2,10} is different than would be expected, based solely on their chemical properties.

The second step, formation of the actual volatile species and/or its release from the liquid phase, is much slower. Only about 30% of the volatile species is released prior to or upon contact of the reaction mixture with the GLS surface. The volatile species precursor is probably present in the solution, and may be concentrated close to the surface of the liquid by a surfactant-assisted process similar to flotation,²¹ sticking to the fine hydrogen bubbles formed in the waste liquid. The volatilization of Ag from the liquid pool requires the presence of decomposing NaBH₄, either as the agent for further reduction, as a source of atomic (nascent) hydrogen, or simply as a source of very fine gas bubbles assisting release of the volatile

compound. In the present design this is fulfilled, as the reaction mixture is dispersed over the walls of the GLS and liquid pool before decomposition of the NaBH₄ is finished.

The precursor can be retained on the walls of the GLS wetted by the pool; the retained portion can be released into the liquid and, upon contact with fresh reaction mixture, produces volatile Ag species. This process is responsible for the long washout times. As well, the slow accumulation of Ag deposits on the surface may be the cause of the long initial conditioning period of the system after cleaning, after which a steady-state sensitivity can be achieved.

Transport and trapping of volatile Ag species

Volatile metal species are reportedly considered to be unstable species,^{3,5,7,11} but reports on actual transport losses differ to a great extent. Less than 10% losses were reported for Ag using a 30 cm transfer line,⁸ as well as a 7.8-fold signal decrease when doubling the transfer line length to 46.8 cm.⁶ Obviously, the transfer tube diameter and surface quality, as well as carrier gas flow rate, play a crucial role. For other elements, severe¹¹ to moderate^{3,6,7} or low² losses of volatilized analyte in the transfer line were reported.

Our experiments do not confirm the fast decomposition of the species. Firstly, experiments with various spray chambers positioned between the CVG and the torch did not indicate any dramatic analyte losses. Moreover, other experiments concerning the transport were performed. A water trap was inserted between the spray chamber and the ICP torch, and the results were compared with the sensitivity without the water trap. If the water level in the trap was below the introduction capillary tip (so that the gas did not bubble through the water), 80% of the Ag, 75% of the Mg and 60% of the Na signals, respectively, were observed, in contrast to only 35 % for selenium. If the gas was bubbled through the water, as much as 45% of the Ag, 40% of the Mg and 30% of the Na signals were still observed, in contrast to only 6% of the Se signal. This clearly highlights the difference between the rather hydrophobic nature of the volatile Ag species and selenium hydride, which is readily soluble in water. Another point is the remarkable stability of Ag species, once released to the gas phase. The source of the difference between the signal reduction for Na and Mg is not clear, as both are considered to be elements carried over with the aerosol.

If a 0.45 μm PTFE filter is inserted into the gas path, the signals for Ag, Mg and Na completely disappear, while that for Se remains unchanged. This may indicate the presence of a very unstable, simple gaseous Ag compound decomposing on the filter surface. However, this is not in accord with the rather good ability of the volatile Ag species to pass through a water trap (see above).

A more plausible explanation is that the volatile Ag species are, in fact, part of the condensed phase carried by the gas, either volatilized as small particles by themselves (or with adsorbed surfactant), forming such particles on decomposition or being attached to the aerosol droplets. The condensed phase is probably removed from the gas phase by turbulent forces within the small volume of the filter body, rather than being retained as a consequence of the physical size of the filter pores.

CVG efficiency

The determination of the amount of silver retained on the filter is a direct measure of the minimum CVG efficiency (*i.e.*, efficiency of the volatile species generation, release and transport). The PTFE filter was connected directly to the GLS exit, and after the CVG process, the Ag retained on the filter, remaining on the GLS/waste tubing walls, and in the waste liquid, was determined.

In the cleaned, unconditioned system, 11% of the Ag was found on the filter, 33% was adhering to the inside of the GLS and 48% remained in the waste liquid. If the CVG system was conditioned and a steady-state sensitivity was achieved prior to the experiment, the filter retained 28% of the introduced silver and only 29% remained in the liquid phase (Ag retained within the CVG system could not be determined, as additional Ag had been introduced during the prior conditioning step). In a separate experiment, the filter was placed downstream of the spray chamber, at the point where the ICP torch injector tube is typically connected. In a well conditioned system, 22% of the Ag was found on the filter (26% in the waste liquid), reflecting the overall Ag introduction efficiency and also transport losses in the spray chamber. Unfortunately, high blank values for Mg leached from the filters did not allow for an assessment of the efficiency of aerosol carryover.

Identity of the volatile species

At present, there is no published proof of identity of the volatile metal species formed during CVG processes. In accordance with reports on volatile metal species,^{3,4,6} no AAS signal was obtained without the diffusion flame, demonstrating that cold vapors (atoms) of Ag are not produced as a result of CVG, as is the case for Hg, and possibly for Cd.

The most popular hypothesis for the existence of metal hydride molecular species, however, is not well supported by our observations, especially the transport experiments. Generally, the transport experiments suggest greater similarity of the Ag species to aerosol elements than to hydride forming elements (Se). In this study, volatile Ag species are able to pass a rather long and tortuous path, such as various spray chambers and, in contrast to selenium hydride, even the water trap. On the other hand, they are completely retained by the 0.45 μm PTFE filter, on which selenium hydride does not exhibit any loss. The only possible explanation, including the existence of unstable molecular species (hydride), would be that they decompose very quickly on the aerosol droplets/particles, on which they are transported. The difference between the Ag and aerosol element retention in various arrangements could be explained by the aerosol size distribution and different mechanisms of origin: the aerosol element content of a droplet is proportional to its volume, whereas the content of Ag trapped in it would be proportional to its surface area. Obviously, smaller droplets with higher surface to volume ratio, and thus higher relative Ag contents, would be lost less efficiently than bigger ones having a lower surface to volume ratio. This would manifest itself as relatively lower Ag signal attenuation compared with elements transferred as a classical aerosol, which was actually observed.

The other possibility is that Ag is volatilized in the form of very small metal particles, which are known to be formed in solution following Ag^+ reduction by tetrahydroborate,²² and also stabilized by surfactant.²³ The particles interact with the surfactant, which is present at a concentration about one order of magnitude smaller than the CMC, and become hydrophobic. The hydrophobized particles attach to the fine hydrogen bubbles originating from decomposition of the tetrahydroborate, and are stripped from solution (such Ag particles may even induce the formation of bubbles). Once in the gas phase, the particles would behave in a manner similar to the aerosol fraction, although the former are probably of much smaller size.

An attempt to identify the volatile Ag species was undertaken using an electrospray ionization (ESI) mass spectrometer. The gas phase from the CVG was connected to the auxiliary gas inlet of the ESI source. However, no species containing silver were found in the resulting spectrum. The only species detected were identified as Triton-X100, probably because this compound has very good ionization yield in this

source. Other ionization sources may probably be needed for successful identification of the Ag species. In case the volatile species are in fact Ag particles, the possibility of their detection is limited by the fact that a particle of 1 nm diameter would contain around 30 atoms (based on the density of silver metal and on interatomic distance of 0.25 nm in silver nanoparticles²⁴), which means a m/z around 3240 for a singly charged particle. Larger particles may be present beyond the mass range of the instrument, unless multiple ionization states are achieved.

Conclusions

The CVG of transition metals has proved to be a viable technique for efficient introduction of analyte for atomic spectrometric techniques. There is definitely potential for further improvement. Unfortunately, at least for silver, its analytical use is still plagued by pronounced memory effects, arising from the complex CVG processes involving many chemical and physical factors which are not yet completely understood. The current study has raised more questions than answers. Positive identification of the volatile species remains essential for further progress, which can possibly be obtained by either mass-spectrometric methods or those used to characterize particles.

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