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#### Publisher's version / Version de l'éditeur:

https://doi.org/10.1039/b403189j Journal of Analytical Atomic Spectrometry, 19, 8, pp. 1014-1016, 2004

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#### TECHNICAL NOTE

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## Chemical vapour generation of silver: reduced palladium as permanent reaction modifier for enhanced performance<sup>†</sup>

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Received 1st March 2004, Accepted 10th May 2004 First published as an Advance Article on the web 15th July 2004

Permanent modification of the surface of a continuous flow system by reduced metals was studied for chemical vapour generation (CVG) of silver. Both nickel and palladium were found to be active, but only palladium has sufficient stability and chemical resistance for routine use. Single introduction of the modifier to the CVG system is sufficient to avoid long conditioning periods following cleaning and to achieve permanent stabilization of the sensitivity for Ag at a value 3–4-fold higher than in a clean system prior to modification. A possible mechanism responsible for improvement is proposed: the modifier catalyzes the reaction of residual NaBH<sub>4</sub> in the reaction mixture, necessary for the final phases of volatile compound formation and/or its release from solution.

#### Introduction

Chemical vapour generation (CVG) of transition and noble metals by NaBH<sub>4</sub> reduction as a sample introduction method for atomic spectroscopy is the latest development in the well established technique of hydride generation (HG).<sup>1-6</sup> The advantages as well as the limitations and prospects of CVG were thoroughly discussed in a recent review.<sup>7</sup> There are indications that the CVG process consists of two steps:<sup>1,8</sup> the first one very fast, probably corresponding to reduction of the analyte to the metal; the second rather slow, possibly the actual formation and/or release of volatile species. A hypothesis has been formulated that the actual "volatile" species are nanoparticles of the metal released into the gas phase rather than a volatile hydride.<sup>1</sup>

A significant problem noted in CVG is drift in sensitivity.<sup>1,3,8</sup> In a recent study,<sup>1</sup> a very low CVG efficiency was obtained when using a freshly cleaned CVG system; the Ag signal slowly and gradually increased over several blank/standard generation cycles, typically around 5, before achieving steady-state performance that could be reflected in a sensitivity, which was 4or more fold higher than its initial value.

Published studies agree that a fast and efficient reduction is one of the crucial factors in achieving an efficient CVG process.<sup>1,3</sup> An enhanced rate of decomposition of NaBH<sub>4</sub> in the presence of transition metals (Cu, Co, Ni, Au) was verified in several interference studies concerned with HG techniques;<sup>9–11</sup> it appears that the active agent is a product of reaction of metal ions. Nickel, Co and Ru particles were also shown to be efficient catalysts for decomposition of NaBH<sub>4</sub> as a source of hydrogen in fuel cell research.<sup>12</sup> A positive interference from Co and Ni<sup>13,14</sup> on the determination of Zn *via* CVG was observed, with no apparent explanation. It is likely that a Pd-modified CVG of Au was described by Ma *et al.*,<sup>15</sup> although the active agent was believed to be diethyldithiocarbamate (DDTC) and palladium merely an agent immobilizing DDTC onto the reaction coil surface.

† Electronic supplementary information (ESI) available: diagram of chemical vapour generation apparatus. See http://www.rsc.org/ suppdata/ja/b4/b403189j/ This work is an extension of a previously published mechanistic study on the continuous CVG of Ag.<sup>1</sup> It proposes both a remedy for some of the difficulties encountered, *i.e.*, avoidance of pronounced sensitivity drifts and increase in the CVG efficiency through modification of the inner generator surface by deposits of finely reduced metal (Ni or Pd), as well as providing deeper insight into the mechanism of the process.

#### **Experimental**

#### Instrumentation

An IRIS axial plasma ICP-OES spectrometer (Thermo Jarrell Ash Corp., Franklin, MA, USA), having an echelle grating polychromator and CID detector, was used. The operating conditions were as follows: rf power 1150 W; plasma gas 151 min<sup>-1</sup>; intermediate (auxiliary) gas flow rate 11 min<sup>-1</sup>. The following lines were always simultaneously monitored: Ag 328.068 nm (in 79th order), Mg 279.553 nm (93rd), 280.270 nm (93rd) and 285.213 nm (91st); Se 196.090 nm (132nd); Na 330.237 nm (79th); Pd 340.458 nm (77th).

#### CVG system

The continuous flow CVG system was described in detail elsewhere.<sup>1</sup> The core of this system consists of three concentric capillaries: two inner ones (id 0.25 mm and 0.53 mm) are made of deactivated fused silica and used for the introduction of sample/standard and reductant solutions, respectively; the outermost one (id 1 mm) is made of PTFE and serves to introduce a purge gas (150 ml min<sup>-1</sup> Ar). The ends of the capillaries all terminated 1 mm apart. The three concentric capillaries enter the glass gas-liquid separator (GLS), which is identical to a commercial HG on a PerkinElmer FIAS 200 (Bodenseewerk PerkinElmer, Germany). A diagram of the entire CVG system is presented in the electronic supplementary information<sup>†</sup> or the reader is referred to<sup>ref. 1</sup>. The system was mounted such 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 using a peristaltic pump supplied with the spectrometer, fitted with 0.76 mm id Tygon tubing and operating at flow rates of 0.4 ml min<sup>-1</sup>. A separate peristaltic pump (Gilson Minipuls II, Villiers le Bel, France), fitted with 2.29 mm id Tygon tubing, was used for removal of waste solution from the GLS.

The CVG connection to the plasma torch required a speinterface to permit the addition of a make-up gas (Ar  $350 \text{ ml min}^{-1}$ ) while retaining the larger aerosol droplets, and was mounted at a right angle to the CVG system.<sup>1</sup>

#### Reagents

For details on reagents and gases see ref. 1. A 5  $\mu$ g ml<sup>-1</sup> Ni in 0.3 M HNO<sub>3</sub>, 20  $\mu$ g ml<sup>-1</sup> Pd in 0.3 M HNO<sub>3</sub> and 0.25  $\mu$ g ml<sup>-1</sup> Ag, 1  $\mu$ g ml<sup>-1</sup> Mg and 5  $\mu$ g ml<sup>-1</sup> Se mixed standard solution in 0.6 M HNO<sub>3</sub> containing 20  $\mu$ g ml<sup>-1</sup> Triton X-100 was used throughout. 1.2% (m/v) NaBH<sub>4</sub> solution containing Antifoam B (in final dilution of 1 : 7500 (v/v)) was used as reductant.

#### Procedure

The CVG system was cleaned by filling it with *aqua regia* for 5 min followed by rinsing with DIW. At least 3 blank–standard (6 ml each) cycles were measured before the modification to establish a reference sensitivity. Afterwards, modification was performed by CVG on a 4 ml volume of a 20 mg  $1^{-1}$  solution of Pd under the same conditions as for CVG of Ag. Blank–standard cycles were then measured repeatedly. Signals were monitored using a 27 s integration time (total time 45 s per measurement), repeated continuously.

#### **Results and discussion**

#### Nickel as the modifier

Preliminary experiments with CVG of Ni (5  $\mu$ g ml<sup>-1</sup>) using the same experimental setup yielded a very unstable and gradually increasing response, together with a gradual increase of reaction blank intensity (unpublished results). However, the signal from standard solutions of Ag increased approximately 3–4-fold following the introduction of the Ni standard solution (5 mg l<sup>-1</sup>) to the unconditioned CVG system. The sensitivity for Ag then corresponded to approximately the value obtained in a well-conditioned system. Carryover of Na and Mg, *i.e.*, elements which are supposedly not reduced and are transported in the aerosol droplets, increased to a similar extent. Visually, a black deposit could be observed on the walls of the GLS.

It should be noted that this effect is permanent: it persists after the introduction of  $Ni^{2+}$  is stopped. Unfortunately, treatment of the GLS with Ni did not provide sufficient stability: even dilute HNO<sub>3</sub> easily removed the deposits and the Ag signal subsequently decreased. This is not useful for practical purposes as, for example, an accidental interruption of the reductant flow permitting only nitric acid blank to enter the GLS would immediately reverse the Ni treatment and the Ag signal would decrease. Additionally, the Ni treatment would effectively preclude the trace analysis of Ni, an element commonly determined by CVG.

#### Palladium as the modifier

The signal obtained for Ag following the modification of the inner CVG surface with Pd was approximately 3–4-fold higher than that observed under the same conditions prior to the introduction of Pd, as shown in Fig. 1a. By contrast, response for Se was practically unchanged (Fig. 1a), consistent with the fact that SeH<sub>2</sub> is generally accepted to be produced with an efficiency close to 100% using an efficient HG system,<sup>16</sup> and therefore the signal cannot be further increased. On the other hand, a Pd modified surface does not cause permanent reduction in the selenium signal either, despite what may be expected



**Fig. 1** Influence of Pd modification on the CVG signal from introduction of a mixed Ag–Se–Mg standard solution. Traces shown for: a, Ag ( $0.25 \ \mu g \ ml^{-1}$ ), Se ( $5 \ \mu g \ ml^{-1}$ ), Pd ( $20 \ \mu g \ ml^{-1}$ ); b,Mg ( $1 \ \mu g \ ml^{-1}$ ), Na (from NaBH<sub>4</sub> only); double arrow indicates the point of introduction of Pd.

as a consequence of the well-known interference from transition metals with "classical"  $\mathrm{HG.}^{16}$ 

The signal arising from the "aerosol" elements (Na and Mg) was enhanced by approximately the same extent as the Ag signal and a good correlation between changes in the Ag and Mg signals is evident. Silver, however, appears not to be transported simply as an aerosol, as was established from comparisons of the transfer efficiencies for Mg and Ag.<sup>1,3,4</sup> In this study, overall CVG efficiency for Ag was assessed to be 100-fold higher than the transfer efficiency for Mg (based on a comparison of sensitivities with sample nebulization), and was 30-fold higher than the nebulization efficiency for Ag when using a cross-flow nebulizer for sample introduction (420 cps per ng s<sup>-1</sup> Ag at 328.1 nm line for CVG procedure compared with 14 cps per ng Ag for nebulization). This suggests that the decomposition of NaBH<sub>4</sub> after modification of the CVG surface becomes faster and more violent, thereby producing more/finer aerosol spray. It also suggests that the release of the volatile Ag species proceeds in a fashion similar to that of aerosol formation.

A single application of the Pd coating (CVG from 4 ml of 20  $\mu$ g ml<sup>-1</sup> Pd, *i.e.*, total of 80  $\mu$ g Pd) was found sufficient. Further applications of Pd did not change the CVG characteristics. The Pd coating appears to be stable; no gradual sensitivity decrease was experienced and no signal from Pd could be measured when 0.3 or 0.6 M HNO<sub>3</sub> was used as reaction medium, while an intense but unstable Pd signal was present in the course of the coating phase. The modifier coating from the GLS can be removed by leaching in *aqua regia* for

5 min; the Ag signal then returns to values typical for a clean CVG system.

Experiments were performed in an effort to identify the localized area that may be contributing most to the CVG modification. The CVG generator was modified by Pd and a stable Ag signal was established; subsequently, the area of the residual liquid pool was carefully drained and leached by aqua regia. A signal decrease to 40% of its previous value was experienced. When the whole interior of the gas-liquid separator was cleaned, only 12-15% of the original signal intensity remained-comparable to that achieved with a clean untreated CVG system (the vicinity of the capillary junction was not cleaned). Upon remodification by CVG from 4 ml of 20  $\mu$ g ml<sup>-1</sup> Pd, the sensitivity was nearly restored (to approximately 85% of the original value). This indicates that the modification site consists of active sites on the GLS walls and within the pool of residual liquid, i.e., it influences the second step in the formation/release of volatile Ag species.<sup>1</sup>

In the same experiment, signals decreased to 27 and 11% for sodium and to 60 and 34% for magnesium, respectively. The different impact for these two elements, both carried over as aerosol, is probably a consequence of a change in the origin of the aerosol: Mg containing aerosol is predominantly produced by nebulization at the capillary tip (less influenced by the modifier), whereas sodium originates from decomposition of the NaBH<sub>4</sub>, which is enhanced in the later phase by the modification process.

The supposed modifier action likely occurs via formation of very fine deposits of metallic particulates. Such deposits are either formed deliberately from introduction of the metallic modifier, or gradually from the presence of reduced analyte (as much as one third of deposited Ag was found inside the  $GLS^{1}$ ). Various surface materials may exhibit better or poorer support for these deposits, which may result in very different CVG performance, as observed by Feng et al.<sup>8</sup> It should be noted that the sensitivity for Ag established after Pd modification corresponds approximately to the steady-state sensitivity obtained after about 5 blank/Ag cycles without deliberate modification; this might arise because the surface of such modifier particles becomes coated by a layer of reduced silver. This is further supported by the fact that immediately after introduction of Pd, a high signal for Ag was occasionally observed, and this was followed by a rapid decrease to the "steady-state" value (cf. Fig. 1a-silver may have slightly worse modifier properties than palladium).

Metal particles are known to catalyze the decomposition of <sup>9–12</sup> Controversy remains over whether the mechanism NaBH<sub>4</sub>.<sup>5</sup> of formation of volatile hydrides proceeds via direct reduction by tetrahydroborate, or if the reducing agent is nascent hydrogen released by its decomposition<sup>17</sup> (although recent studies are inclined to a non- nascent hydrogen mechanism<sup>18-20</sup>); the situation is even more obscure in the case of volatile metal species generation. The nascent hydrogen mechanism would be consistent with the enhancement of CVG by metallic modifiers due to higher concentrations of nascent hydrogen formed as a consequence of accelerated decomposition of tetrahydroborate. Direct reduction of analyte by the tetrahydroborate might also be accelerated in the presence of fine metallic particles. As is shown above, the enhancement mechanism is active in the second step, proceeding predominantly in the residual pool of liquid present in the GLS. Likely, the modifier aids the decomposition of any remaining tetrahydroborate essential for the release of volatile species.<sup>1</sup> This is confirmed by the fact that 48% of the Ag was found in the waste liquid after the reaction in an unconditioned system compared to 29% in the well-used system (containing Ag deposits).<sup>1</sup> Unfortunately, the exact mechanism of the first and second step, as well as the identity of the actual volatile species, remains unknown.

If the deposits of analyte inherently influence (positively) the CVG signal, a stable chemical modifier may also permit the use of higher acidity, which would normally remove the deposits formed by the analyte itself, especially those of less chemically resistant analytes such as Ni. In other words, this modification should permit a wider range of optimum experimental conditions.

Finally, the enhanced rate of the tetrahydroborate reaction after modification might also appear beneficial for "classical" HG, as it may allow the use of substantially lower concentrations of the reductant, thereby yielding lower blank values and decreased salt load for detectors such as AFS or ICP-MS.

#### Acknowledgements

T.M. is grateful to NSERCanada for a Visiting Fellowship. This work was supported by NRC and by GACR grant No. 203/01/0453. The authors thank Jiří Dědina for useful discussions and Victor J. Boyko for his assistance.

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