Chemical Vapor Generation — Electrothermal Atomic Absorption Spectrometry: New Perspectives

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Chemical vapor generation—electrothermal atomic absorption spectrometry: new perspectives

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Abstract

Volatile species of Ag, Cu, Cd, and Zn were generated at room temperature by the addition of sodium tetrahydroborate (III) to an acidified solution of the analytes. The vapor-phase species were rapidly transported to a pre-heated graphite tube, the surface of which was previously treated with Ir as a permanent chemical modifier. The volatile species were trapped at the Ir treated tube surface, and the further heating of the furnace permits their determination by atomic absorption spectrometry. A univariate approach was used to achieve optimized conditions and derive the figures of merit. The limits of detection based on a 3σ criterion were 10 (1); 0.006 (6×10⁻⁵); 28 (2.8) and 1.1 (0.11) ng (µg ml⁻¹) for Ag, Cd, Cu and Zn, respectively. Precision of replicate measurements was typically approximately 10% R.S.D. Using a transfer line as short as possible should minimize losses of analyte during the transport to the graphite furnace. The overall efficiency of the volatile species generation and trapping process estimated for silver was 13%.

Keywords: Chemical vapor generation; Electrothermal atomic absorption spectrometry; Metal transition volatile species; In situ trapping; Iridium modifier
1. Introduction

In-situ graphite furnace trapping procedures are particularly attractive for the determination of very low concentrations of hydride forming elements. They currently provide a sensitive atomic spectroscopic technique available for the determination of As, Cd, Ge, Pb, Se, Sb and Sn [1–6]. Despite its simplicity and ease of application, this approach implies the need for a well-developed porous graphite structure at the tube wall for optimum trapping efficiency and high deposition temperatures for some elements [4]. Due to their properties, the platinum group metals, particularly Pd, Ir and Rh, alone or together with carbide forming elements (Rh, Ru) [7,8], may act as permanent modifiers [7,8], permitting the entrapment of hydride forming elements as well as Hg. Palladium is recognized as a more efficient collector compared with other platinum group metals (PGM) [9]. However, Welz et al. [10] showed that Pd might be used as a permanent modifier only if the furnace temperature does not exceed 1500 °C. Unfortunately, the majority of elements commonly determined by electrothermal atomic absorption spectrometry (ETAAS), including the hydride forming ones, require atomization temperatures higher than 1500 °C. The use of other PGM permits higher atomization temperatures without losing their trapping-efficiency [7]. Silva et al. [11], for instance, showed that the use of iridium, rhodium or a mixture of both as a permanent modifier in the determination of Ag, As, Bi, Cd and Sb is advantageous in comparison to the use of the modifier in solution.

Luna et al. [12] investigated the variables that influence the vapor generation of Ag, Au, Cu and Zn, following the batch reduction of the analyte solutions with tetrahydroborate(III) and detection of the generated volatile species in a heated quartz tube atomizer (QTA), mounted in an atomic absorption spectrometer. However, the use of a QTA as atomization cell results in the dilution of the hydrides by the evolved hydrogen and the carrier gas, decreasing the sensitivity of the determination. Moreover, temperatures above 1000 °C can usually not be obtained in heated quartz tubes, and this atomizer is sensitive to gas phase interferences [13]. In order to improve the sensitivity Matousek et al. [14] recently investigated the use of a diffusion flame and a multiple micro-flame quartz atomizer for the atomization of volatile Ag species generated by a continuous flow system.

The aim of the present work is to investigate the feasibility of in-situ trapping procedures for the determination of Ag, Cd, Cu and Zn by ETAAS, after generation of their respective volatile species by reaction of their aquo-ions with sodium tetrahydroborate(III) in a micro batch reactor.

2. Experimental

2.1. Instrumentation

Measurements were carried out with a Perkin-Elmer (Norwalk, CT, USA) Model 1100 atomic absorption spectrometer equipped with a deuterium-arc lamp background corrector, and an HGA-300 graphite furnace. All measurements were based on integrated absorbance. Hollow cathode lamps (Intensitron, Perkin-Elmer) were used as line sources. Pyrolytic graphite coated polycrystalline electrographite tubes (Perkin-Elmer part no. BO10-9322) were used throughout. The operating parameters and the instrumental settings were according to the manufacturer’s recommendations. The absorption peak profiles were printed out using a Perkin-Elmer EX–800 printer. The volatile species were introduced into the graphite tube via a glass capillary tube (18 mm long×1 mm i.d.), held by the autosampler arm, and connected to the outlet of the micro batch reactor by a PTFE tube (100 mm long×1.6 mm i.d.). The miniature batch system used for the chemical vapor generation is described in Luna et al. [12]. A schematic diagram of the montage used for the collection in the graphite tube is presented in Fig. 1.

2.2. Materials and reagents

Argon (99.96%, Aga, Rio de Janeiro, Brazil) was used as purge and protective gas. Milli-Q water (resistivity of 18.2 MΩ cm) was used throughout and all chemicals were of analytical reagent grade, unless otherwise specified. Sub-
boiled HCl was obtained from a quartz sub-boiling apparatus (Hans Kuerner, Rosenheim, Germany). Silver, cadmium, copper and zinc stock solutions (1000 mg l⁻¹) were prepared by adequate dilutions of their respective Titrisol® concentrates (Merck, Darmstadt, Germany). Analytical solutions were freshly prepared by convenient dilution of the 1000 mg l⁻¹ stock solutions with diluted sub-boiled HCl. Sodium tetrahydroborate (III) solutions were prepared by dissolving the salt (Merck, Rio de Janeiro, Brazil) in 0.1% m/v sodium hydroxide solution. This solution was daily prepared and always filtered before use. Ir was deposit onto the graphite tube wall using a 5000 mg l⁻¹ solution prepared from adequate dissolution of its chloride salt (Fluka AG, Buchs SG, Switzerland) in 10% v/v nitric acid. All plastic and glassware were cleaned by immersion in 10% v/v HNO₃ for at least 24 h and thoroughly rinsed with Milli-Q water before use.

2.3. Procedures

2.3.1. Tube coating

The iridium coating procedure is described in detail in previous work [7]. In summary, 20 μl of the 5000 mg l⁻¹ solution were introduced into the tube and submitted to the temperature program shown in Table 1. This procedure was repeated six times, resulting in a deposited Ir mass of 600 μg.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temp. (°C)</th>
<th>Ramp (s)</th>
<th>Hold (s)</th>
<th>Ar flow rate (ml min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>20</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>20</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>2300</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>2500</td>
<td>5</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>5</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

*a Read in this step.

2.3.2. Metal collection and atomization

The sequence of operation for collection and atomization of the volatile metal species was as follows: 10 μl of the analyte solution was injected in the center of the fritted glass surface of the micro batch reactor. This procedure was performed manually using an Eppendorf microliter pipette, fitted with a disposable polypropylene tip. The graphite furnace was heated to 300 °C, and as soon as this temperature was reached, the glass capillary tube attached to the autosampler arm was inserted manually into the graphite tube. The NaBH₄ solution was pumped to the micro batch reactor (5 s, 1 ml min⁻¹), initiating the generation and collection of the volatile species. Once the collection period was completed, the glass capillary was removed from the graphite tube, and the analyte was atomized according to the temperature program shown in Table 2. The optimum atomi-
Table 2
Temperature program for the trapping and determination of Ag, Cd, Cu and Zn

<table>
<thead>
<tr>
<th>Step</th>
<th>Temp. (°C)</th>
<th>Ramp (s)</th>
<th>Hold (s)</th>
<th>Ar flow rate (ml min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>10</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>1</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>Atomization*</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>2500</td>
<td>4</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>10</td>
<td>5</td>
<td>300</td>
</tr>
</tbody>
</table>

* 1600 was used for Cd and Zn, 1800 for Ag and 2200 for Cu.
* Read at this step.

zation temperatures were obtained from temperature curves, and are shown in Table 2. A cleaning step of 2500 °C (10 s) proved to be sufficient for all studied elements.

3. Results and discussion

3.1. Preliminary tests

3.1.1. Investigation of the possibility of transporting the analyte by aerosol formation

In a deliberate attempt to induce aerosol formation without the possibility of volatile species production, the ‘generation’ reaction was simulated by replacing the NaBH₄ by a Na₂CO₃ solution. A rapid release of CO₂ following the addition of this reagent to the acidic sample solution was observed. Thus, similar quantities of the analyte would be transported to the graphite furnace if aerosol formation were a significant transport mechanism. However, no signals were obtained for any of the studied analytes, proving that liquid aerosol transport plays no role during the NaBH₄ reduction.

3.1.2. Effect of the transfer line dimensions and materials on the Ag signal

In order to investigate the influence of the inner diameter of the Teflon transfer line on the analyte signal, two 10-cm lengths of Teflon tubing with inner diameters of 1.64 mm (line I) and 3.91 mm (line II) were investigated. Silver was used as a test element, and the surface-to-volume ratio given by \((\text{surface}/\text{volume})_\text{line II}/(\text{surface}/\text{volume})_\text{line I}\) was 0.42. Indeed, a line II/line I signal ratio of 0.38 was observed, indicating that the generated analyte vapor losses to the inner surface of the transfer line must be considered.

In order to investigate the effect of the transfer line length and material, two different Teflon lines with the same inner diameter (1.64 mm) were used: line I, 10 cm long, and line II, 20 cm long. Silver was used as the test element. Doubling the length of the transfer line caused a 7.8-fold decrease in the peak area response. Changing the Teflon by a Tygon tubing of the same dimensions led to a 46-fold signal attenuation. This behavior illustrates the significant impact of the tubing surface reactivity on the loss processes rather than a spontaneous decomposition of the formed volatile species during the transport.

3.1.3. Determination of the formation and release efficiencies

The efficiency of the overall measurement process, \((\Pi \varepsilon)\), is determined by a number of factors impacting the efficiency of species generation (\(\varepsilon_g\)), gas/liquid separation (\(\varepsilon_g\)), transport of the vapor to the graphite furnace (\(\varepsilon_t\)), trapping of the vapor on the graphite surface (\(\varepsilon_n\)), and atomization (\(\varepsilon_a\)):

\[ \Pi \varepsilon = \varepsilon_g \varepsilon_t \varepsilon_n \varepsilon_a \]

The efficiency of the generation was estimated for Ag from measurements of its residual amount in the remaining solution after the generation of the analyte vapor from a solution containing 100 ng of the metal. The remaining solution was transferred to a 15-ml flask and the micro-batch reactor was thoroughly washed with several portions of a concentrated HNO₃ diluted 1:1 with water, which were also transferred to the same flask. The solution was made up to the mark with water, and its analysis by conventional ETAAS revealed that 80% of the Ag had been converted to a volatile form and liberated from the reaction cell. The atomization of the same Ag mass (100 ng) by conventional ETAAS revealed that 84% of the volatile Ag species was either retained in the transfer line or not trapped on the Ir treated surface.

3.1.4. Internal furnace gas flow during concentration step

The study of the influence of the gas flow rate through the furnace during the trapping step
showed that the highest signals were obtained in the stopped flow mode.

3.2. Systematic optimization of the experimental parameters

The effect of various physical and chemical parameters was investigated in order to identify their value providing the maximum sensitivity. This optimization was performed using a univariate approach. The parameters not studied were kept at arbitrary values, while the studied one was investigated. A second round of experiments was performed, fixing the non-studied parameters at the optimum values found in the first round. The values finally considered as optimum were taken from this second approximation.

Each experiment was performed with the analyte in aqueous solution, acidified with hydrochloric acid. Some restrictions due to the limitations of the equipment had to be considered: The argon flow rate could not exceed 8 ml min\(^{-1}\) and the sample volume could not go beyond the limit of 50 µl otherwise some liquid could inadvertently be flushed from the micro batch reactor into the transfer line. Moreover, the NaBH\(_4\) concentration could not exceed 1% m/v. The use of higher values resulted in the production of too large quantities of H\(_2\), resulting in significant signal instability. Indeed, several droplets of solution were observed at the top of the micro batch reactor for larger NaBH\(_4\) concentrations. Thus, these variables were investigated just up to these values.

3.2.1. HCl concentration

The influence of the HCl concentration on the Ag, Cd, Cu and Zn signals was investigated. The results are presented in Fig. 2. The optimum HCl concentration was 0.6 mol l\(^{-1}\) for Cu and 1.2 mol l\(^{-1}\) for Zn. For Cd, the signal was maximum in the 0.6–1.2 mol l\(^{-1}\) range, while for Ag, a plateau was observed for HCl concentrations ranging from 1.2 to 2.4 mol l\(^{-1}\). In order to keep the blank as low as possible, the 1.2-mol l\(^{-1}\) HCl concentration was chosen for the Ag determination. For Zn, the analysis of the signal to noise ratio determined the choice of the same HCl concentration.

3.2.2. NaBH\(_4\) concentration

Concerning the influence of the NaBH\(_4\) concentration, maximum signals were reached at a NaBH\(_4\) concentration of 1% m/v for all analytes.
As explained before, larger NaBH₄ concentrations led to the transport of droplets into the transfer line. No significant influence of this parameter was observed on the repeatability of the measurements; hence, 1% m/v was chosen for the NaBH₄ concentration.

3.2.3. Carrier gas flow rate

The influence of the carrier gas flow rate on the Ag, Cd, Cu and Zn signals is presented in Fig. 3. For Cu, a nearly constant response was observed for flow rates ranging from 2 to 8 ml min⁻¹, suggesting that optimum conditions have been achieved. In the case of Cd and Zn, an increase in the carrier flow rate from 4 to 8 ml min⁻¹ caused a steep increase in the analytical signal. Probably larger carrier gas flow rates cause a more effective sweeping of their volatile species from the reaction solution. Another possible explanation is that larger flow rates reduce the residence time of the volatile species in the transfer line, lowering the risk of their retention on the inner surface of the transfer line.

3.2.4. Reaction and trapping time

Reaction and trapping times are intimately related and can only be treated together. Fig. 4 shows that there is no simple correlation between this parameter and the absorbance signal. The fast increase of the response between 10 and 20 s indicates that 20 s is necessary for the complete generation and transport of the formed volatile species to the graphite tube at the carrier gas flow rates used (Table 3). For Ag and Cu, there is another 30% signal enhancement if the trapping time is increased from 20 to 80 s. One can speculate that this further signal increase is related to transport efficiency of the volatile species that are otherwise retained in the inner surface of the transfer line. For Cd, the maximum response is obtained at 20 s. From this time on, a plateau at a somewhat lower response level is observed. Zinc also shows a unique behavior, with a maximum between 20 and 40 s, and a rapid drop for larger times. A clear understanding of this behavior claims at more specific experiments. However, it was possible to choose 80 s (Ag and Cu) and 20 s (Cd and Zn) as the optimum reaction/trapping times. Reaction and trapping times over 80 s were not investigated in order to avoid a too slow analytical determination.

3.2.5. Trapping temperature

The influence of the trapping temperature on the normalized response of the studied elements is presented in Fig. 5. A nearly constant signal for Zn was observed in the range of 300–400 °C. For the other elements, a maximum was observed at 300 °C. Therefore, 300 °C was selected as the trapping temperature.

3.2.6. Atomization temperatures

Atomization temperatures of 1600 °C, 1600 °C, 1800 °C and 2200 °C for Cd, Zn, Ag and Cu, respectively, were derived from atomization temperature curves.

3.2.7. Calibration studies and analytical figures of merit

Table 3 summarizes the optimized values obtained for the studied parameters while Table 4 shows some analytical data taken from analytical curves obtained under such conditions. In all cases only integrated peak response was considered. The F-test demonstrated that linear regression was always statistically permissible and this model showed goodness of fit.

It is recognized that the generation/transport system used for this investigation is still not totally optimized, and could be improved. The overall efficiency of the volatile species generation and trapping process estimated for silver was 13%.

For Cd, the corresponding limit of detection based on a 3σₓ criterion was 0.006. This LOD is similar to that obtained by Guo and Guo [4] (0.008 ng), using HG-QT AAS. For Zn, based on the same criterion, the observed LOD was 1.1 ng, very close to that (1.8 ng) found by Luna et al. [12] also using HG-QT AAS. The poor LOD observed for Ag and Cu (9.6 and 28 ng, respectively) are related to their low sensitivities, as demonstrated by the slopes of their respective analytical curves (Table 4). They are similar to those found in a previous work using HG-QT AAS (7 and 17 ng, respectively) [12].
Fig. 3. Effect of Ar carrier gas flow rate on the normalized peak area response: (●) Ag, 50 ng; (○) Cd, 250 pg; (▼) Cu, 50 ng; (▼) Zn, 5 ng.

Precision of replicate measurements is typically of the order of 10% RSD. Considering the magnitude and source of the blank, in addition to the coarse means by which the reagents are mixed, it should be possible to improve substantially this figure, e.g. by automation.

Fig. 4. Effect of reaction and trapping time on the normalized peak area response: (●) Ag, 50 ng; (○) Cd, 250 pg; (▼) Cu, 50 ng; (▼) Zn, 5 ng.
Table 3
Optimized conditions for the determination of Ag, Cd, Cu and Zn

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ag</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol (1^{-1}) HCl in analytical solution</td>
<td>1.2</td>
<td>1.2</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>% m/v NaBH(_4) in 0.05 mol (1^{-1}) NaOH</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Argon flow rate (ml min(^{-1}))</td>
<td>2</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Reaction and trapping time (s)</td>
<td>80</td>
<td>20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Trapping temperature ((^{\circ})C)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Temperature of atomization ((^{\circ})C)</td>
<td>1800</td>
<td>1600</td>
<td>2200</td>
<td>1600</td>
</tr>
</tbody>
</table>

Fig. 5. Effect of trapping temperature on the normalized peak area response: (●) Ag, 50 ng; (○) Cd, 250 pg; (▼) Cu, 50 ng; (▲) Zn, 5 ng.

Table 4
Analytical figures of merit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ag</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (ng(^{-1})s(^{-1}))</td>
<td>0.0005</td>
<td>0.0889</td>
<td>0.0013</td>
<td>0.0349</td>
</tr>
<tr>
<td>Intercept (s(^{-1}))</td>
<td>0.0014</td>
<td>0.0428</td>
<td>0.0245</td>
<td>0.0700</td>
</tr>
<tr>
<td>Upper mass(^a) (ng)</td>
<td>100.0</td>
<td>1.00</td>
<td>100.0</td>
<td>10</td>
</tr>
<tr>
<td>Coefficient of multiple correlation ((R^2))</td>
<td>0.9955</td>
<td>0.9981</td>
<td>0.9916</td>
<td>0.9813</td>
</tr>
<tr>
<td>Coefficient of correlation ((R))</td>
<td>0.9977</td>
<td>0.9990</td>
<td>0.9958</td>
<td>0.9906</td>
</tr>
<tr>
<td>LOD ((3\sigma_n; n = 10)) (ng)</td>
<td>10</td>
<td>0.064</td>
<td>27.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Precision (% R.S.D.) (^b)</td>
<td>17 (50)</td>
<td>9.0 (0.50)</td>
<td>11 (50)</td>
<td>6.1 (5)</td>
</tr>
</tbody>
</table>

\(^a\) Upper mass studied for which the response was linear.

\(^b\) Number in parentheses represent mass of analyte (ng) used for the measurement.
4. Conclusions

The precise composition of the volatile species generated in the presented experiments remains to be elucidated (likely by mass spectrometry). Nevertheless, the evidence presented suggests that rapid generation–separation of a volatile species (probably hydrides) at room temperature from acidic solutions of the studied metal ions occurs at atmospheric pressure. A large influence of the transfer line inner surface (nature and size) was observed, demonstrating that part of the volatile species is retained during transport from the microbatch reactor to the graphite tube. Thus, for further optimization this line must be kept as short as possible. Moreover, other tubing materials must be investigated. The silanization of the inner surface of the transfer line might lead to better transport yields. Sorption processes on the inner surface of the glass tip must be investigated separately, and its dimension and material be optimized. It was also clear that higher NaBH₄ concentrations would result in larger responses, and their use might become possible after an improvement of the micro batch reactor design. Also, the back-and-forth movement of the autosampler arm bends the transfer line tubing, changing the path of the volatile species through it. Considering the losses of volatile species to the tubing material, and its consequences on the repeatability, this movement must be minimized. The exact point of the micro batch reactor fritted glass surface where the sample is deposited also influences the response and an automation of this step might improve the repeatability. As already pointed out, the system is still far from its optimum performance. However, the combination of the chemical generation of the volatile species with in-situ concentration in a commercially available graphite furnace using Ir coated tubes proved to be feasible for the studied elements.

Acknowledgments

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