



Chemical vapor generation of silver for atomic absorption spectrometry with the multiatomizer: Radiotracer efficiency study and characterization of silver species

Stanislav Musil^{a,b}, Jan Kratzer^a, Miloslav Vobecký^a, Jan Hovorka^c, Oldřich Benada^d, Tomáš Matoušek^{a,*}

^a Institute of Analytical Chemistry of the ASCR, v.v.i., Vídeňská 1083, 142 20 Prague 4, Czech Republic

^b Charles University in Prague, Faculty of Science, Dept. of Analytical Chemistry, Albertov 8, 128 43 Prague 2, Czech Republic

^c Charles University in Prague, Faculty of Science, Institute for Environmental Studies, Benátská 2, 128 01 Prague 2, Czech Republic

^d Institute of Microbiology of the ASCR, v.v.i., Vídeňská 1083, 142 20 Prague 4, Czech Republic

ARTICLE INFO

Article history:

Received 1 July 2009

Accepted 23 September 2009

Available online 2 October 2009

Keywords:

Atomic absorption spectrometry

Chemical vapor generation

Multiatomizer radiotracer

Silver

Aerosol size distribution

ABSTRACT

Volatile Ag species were generated in flow injection arrangement from nitric acid environment in the presence of surfactants (Triton X-100 and Antifoam B) and permanent Pd deposits as the reaction modifiers. Atomic absorption spectrometry (AAS) with multiple microflame quartz tube atomizer heated to 900 °C was used for atomization; evidence was found for thermal mechanism of atomization. Relative and absolute limits of detection (3σ , 250 μl sample loop) measured under optimized conditions were: 1.4 $\mu\text{g l}^{-1}$ and 0.35 ng, respectively.

The efficiency of chemical vapor generation (CVG) as well as spatial distribution of residual analyte in the apparatus was studied by ^{111}Ag radioactive indicator (half-life 7.45 days) of high specific activity. It was found out that 23% of analyte was released into the gaseous phase. However, only 8% was found on filters placed at the entrance to the atomizer due to transport losses. About 40% of analyte remained in waste liquid, whereas the rest was found deposited over the CVG system.

Presented study follows the hypothesis that the “volatile” Ag species are actually metallic nanoparticles formed upon reduction in liquid phase and then released with good efficiency to the gaseous phase. Number/charge size distributions of dry aerosol were determined by Scanning Mobility Particle Sizer. Ag was detected in 40–45 nm particles holding 10 times more charge if compared to Boltzmann equilibrium. At the same time, Ag was also present on 150 nm particles, the main size mode of the CVG generator. The increase of Ag in standards was reflected by proportional increase in particle number/charge for 40–45 nm size particles only.

Transmission electron microscopy revealed particles of 8 ± 2 nm sampled from the gaseous phase, which were associated in isolated clusters of few to few tens of nanometres. Ag presence in those particles was confirmed by Energy Dispersive X-ray Spectroscopy (EDS) analysis.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The chemical vapor generation (CVG) of transition and noble metals as a prospective introduction technique for analytical atomic spectrometry has been recently summarized in several reviews [1–4]. This technique is analogous to classical hydride generation (HG) technique: analyte is reduced by sodium borohydride and released into the gaseous phase, which is introduced to the spectrometric detector. Similar virtues as in the case of HG are expected: superb sensitivity given by high introduction efficiency, separation of analyte from the matrix and possibly even analyte collection and preconcentration.

Although successful CVG of about 20 transition and noble metals was described to date including some analytical applications to real samples, the situation is not as simple as in the case of HG. Reliable assessments of CVG efficiency as reviewed in Ref. [5] are scarce and the values are much worse than as in the case of HG, despite the use of reaction enhancers such as complexing agents: 8-hydroxyquinoline and 1,10-phenantroline [6–9] or diethyldithiocarbamate [10,11], surfactants [12,13], finely dispersed metals [14], or, most recently, room temperature ionic liquids [15].

Importantly, the crucial question, i.e. what is the actual identity of volatile metal species, still remains unanswered. Popular belief in “volatile metal hydrides” is not based on any experimental evidence. The hypothesis that “volatile” species are in fact nanoparticles [12,14], which are possibly stabilized by surfactants [12] or room temperature ionic liquids [15] has not been proven yet either. A study of the borohydride reaction with metal ions [16] brought tentative reaction scheme but no conclusion on actual volatile species. Volatile species of

* Corresponding author.

E-mail address: matousek@biomed.cas.cz (T. Matoušek).

Rh, Pd, Au and Cu can be collected by bubbling the gaseous phase through water column and then recovered by sparging to some extent [17]. AAS signals of “cold” atoms of Ag, Pd and Cu in solution [18], possibly present in microbubbles [19] were observed in the course of borohydride reduction. On the other hand, there was never observed signal of free metal atoms (except cadmium and mercury) in the gaseous phase without atomization environment [10,13,20]. Metal speciation studies are also complicated by fact, that CVG procedure itself, even without any heavy metal present, generates aerosol by liquid disintegration. Such liquid droplets evaporate or grow in dependence of liquid vapor pressure in a CVG generator. Vapor pressure characterizes mass equilibrium between gaseous and liquid phases. Due to droplet curvature, the smaller particle diameter the higher vapor pressure is required to maintain the mass equilibrium at constant temperature. Therefore, there is a distinct particle diameter at given vapor pressure and temperature when the particle neither grows nor evaporates. Such particle diameter is called Kelvin diameter. Particles of diameter smaller than Kelvin diameter quickly evaporate and form dry aerosol particles [21]. Generated aerosol, under unchanging concentration of dissolved ionic species and physical parameters, is near monodisperse and acquires characteristic charge [22]. Presence of particles different in charge and size from the main mode generated by simple liquid disintegration, allows identification of other particle-forming processes which undergo during the CVG procedure.

The aim of this paper was to test the performance of Ag CVG procedure with atomization in the multiple microflame quartz tube atomizer (multiatomizer) [23] for AAS including determination of the generation efficiency by the radioactive indicator. This study also follows the hypothesis that the “volatile” Ag species are actually metallic nanoparticles formed upon Ag reduction in liquid phase and then released with good efficiency to the gaseous phase [12]. Therefore, the hypothesized nanoparticles are studied by the use of aerosol characterization techniques as well as electron microscopy.

2. Experimental

2.1. Instrumentation

Perkin-Elmer 503 AAS spectrometer (Perkin-Elmer, Bodensee-werk, Germany) was utilized. Silver hollow cathode lamp (Perkin-Elmer) – 328.1 nm line, 0.7 nm spectral bandpass – operated at 12 mA was the radiation source. Perkin-Elmer 4000 AAS spectrometer with deuterium background correction was used to determine Ag content in specified particle size fractions (see Sections 2.6 and 3.4). Signals from spectrometers' strip chart recorder outputs were AD converted in a PC. Signals were exported as ASCII files into Origin Pro 7.5 (Origin Lab Corp.) software for further processing. Peak areas were evaluated if not stated otherwise. Averages from 3–5 replicate measurements are shown in figures, error bars represent standard deviation.

2.2. Atomizers

The multiatomizer was identical to that described previously (model MM5 in Ref. [23]). The inner tube of the optical bar of the atomizer used in this study was 120 mm long with 7 mm i.d. and fourteen orifices of approximately 0.5 mm in diameter [23]. The atomizer was heated electrically to 900 °C by an in-house made furnace controlled by a REX-C100 controller (Syscon, Indiana, U.S.A.) with a K-type thermocouple sensor (Omega Engineering, U.S.A.). 20 ml min⁻¹ of air as outer gas for the atomizer was used if not stated otherwise. Where stated, original FIAS 200 conventional heated quartz tube atomizer (QTA) with identical inside dimensions of the optical bar was used for comparison.

2.3. System for flow injection chemical vapor generation of Ag

The flow injection CVG system was in detail described elsewhere [12]; schematic illustration of the CVG chemifold is shown in Electronic supplementary information (Fig. S1). It was constructed of PTFE tubing and 1/4-28 threaded PEEK connectors. Sample plug is injected into flow of carrier (0.6 M HNO₃) by a manual injection vent (5020 sample injection valve, Rheodyne, CA, U.S.A.) with 250 μl sample loop. In a T-piece, chemical modifier (see Section 3.1) was added from a separate channel. The core of the system is the mixing manifold based on 3 concentric capillaries and gas–liquid separator. Innermost capillary (non-polar fused silica, 0.25 mm i.d.) leads carrier with sample plug and chemical modifier, middle one (non-polar fused silica, 0.53 mm i.d.) the reductant solution and the outer one (PTFE, 1 mm i.d.) carrier gas – Ar 50 ml min⁻¹ if not stated otherwise. The capillaries end in 1 mm distances and protrude 5 mm inside the gas–liquid separator (GLS; glass, volume 3 ml). A flow of waste stabilizer (0.5 M NaOH) was pumped to the waste outlet from the GLS to stop the residual H₂ evolution within the waste liquid tubing. Liquids were pumped by peristaltic pumps (Reglo Digital 4-11, Ismatec, Switzerland) at the flow rate of 0.5 ml min⁻¹ for reagents if not stated otherwise and arbitrary rate for the waste pump. Gas flows were controlled by mass flow controllers (FMA-2400 or 2600 Series, Omega Engineering). GLS was connected to a miniature double-pass glass spray chamber [12] (Fig. S1), which was then connected to atomizer by a glass piece (30 mm long, 2.5 mm i.d.) with matching round standard joint and Teflon tube (65 mm long, 2.4 mm i.d.). The system was pre-conditioned with CVG from 4 ml of 10 mg l⁻¹ of Pd solution (BDH, UK) as described earlier [14].

For some experiments, continuous flow (CF) version of the system was used. In this case the injection vent was removed and blank (0.6 M HNO₃) or Ag standard was aspirated continuously into the carrier channel.

2.4. Reagents and standards

Deionized water (<0.2 μS cm⁻¹, ULTRAPURE, Watrex, Czech Rep.) was used for all solutions. Working standards (10–500 μg l⁻¹ Ag) were prepared by serial dilution of 1000 mg l⁻¹ stock solution (BDH, UK) in 0.6 M HNO₃ (p.p., Lach-Ner, Czech Rep.), which was also used as carrier liquid. The reductant solution of 2.4% (m/v) NaBH₄ (Fluka, Buchs, Switzerland) in 0.1% KOH (p.a., Lachema, Czech Rep.) with antifoaming agent (132 μl of 10% (m/v) solution of Antifoam B emulsion (Sigma) per 100 ml) [12] was prepared fresh daily. Bubbles of gas were removed from this solution online just before the reaction [12].

The tested reaction modifiers were prepared from Triton X-100 (Serva); 8-hydroxyquinoline; 1,10-phenantroline, K₃[Fe(CN)₆] (all p. a., Lachema).

2.5. ¹¹¹Ag radiotracer experiments

¹¹¹Ag radioactive indicator (half-life 7.45 days) of high specific activity (ca 10 MBq ng⁻¹ Ag) was prepared by bombarding target nuclide ¹¹⁰Pd (palladium powder, 5N purity, Aldrich) with high flux of neutrons in a core of research nuclear reactor (LVR-15 Nuclear Research Institute Řež plc, Czech Rep.) at thermal output of 9.5 MW according to the nuclear processes: ¹¹⁰Pd(n,γ)¹¹¹Pd(β-)¹¹¹Ag. Chemical separation and isolation of ¹¹¹Ag radionuclide followed after decaying of ¹¹¹Pd. Irradiated metallic palladium was dissolved in the mixture of concentrated HCl and HNO₃, the solution evaporated, redissolved in minimum amount of 4M HCl and applied on the column (2.5 mm diameter, 140 mm) of anion exchanger (Dowex 2, X-8, 200–400 mesh; Biorad) in Cl⁻ cycle. ¹¹¹Ag radionuclide was separated by elution by 7M HCl from target palladium and ¹⁹²Ir formed from iridium traces present in target material. Combined

Download English Version:

<https://daneshyari.com/en/article/1240704>

Download Persian Version:

<https://daneshyari.com/article/1240704>

[Daneshyari.com](https://daneshyari.com)