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Sapphire: a better material for atomization and *in situ* collection of silver volatile species for atomic absorption spectrometry ☆

Stanislav Musil *, Tomáš Matoušek, Jiří Dědina

Institute of Analytical Chemistry of the ASCR, v. v. i., Veveří 97, 602 00 Brno, Czech Republic

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ABSTRACT

Sapphire is presented as a high temperature and corrosion resistant material of an optical tube of an atomizer for volatile species of Ag generated by the reaction with $NaBH_4$. The modular atomizer design was employed which allowed to carry out the measurements in two modes: (i) on-line atomization and (ii) *in situ* collection (directly in the optical tube) by means of excess of O_2 over H_2 in the carrier gas during the trapping step and vice versa in the volatilization step. In comparison with quartz atomizers, the sapphire tube atomizer provides a significantly increased atomizer lifetime as well as substantially improved repeatability of the Ag *in situ* collection signals shapes. *In situ* collection of Ag in the sapphire tube atomizer was highly efficient (>90%). Limit of detection in the on-line atomization mode and *in situ* collection mode, respectively, was 1.2 ng ml^{-1} and 0.15 ng ml^{-1}.

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1. Introduction

Volatile species generation of transition metals by the reaction with $NaBH_4$ in acidic medium still attracts the attention as proven by the latest review by Pohl et al. [1]. Some insight into the mechanism of volatile species generation and nature of volatile species (most probably nanoparticles [2,3]) has been gained as well as analytical applications have been extended to various samples. Although, it is still not as simple and mature method as hydride generation [4,5], it brings similar advantages, such as more efficient introduction of an analyte for analytical atomic spectrometry methods. Among these, atomic absorption spectrometry (AAS) is still popular because of its sensitivity-cost ratio.

To atomize volatile species of transition metals for AAS, conventional externally heated quartz tube atomizers have been the most commonly used devices. The quartz tube atomizers, which are primarily designed for hydrides, usually operate continuously (on-line atomization) but enable also collection of an analyte [6] in the inlet arm or *in situ* (*i.e.* directly in the optical tube) similarly as is typical for graphite furnaces [7,8]. The first collection of Pb by hydride trapping in the quartz heated inlet arm (separated or integrated with the quartz tube atomizer) was described by Ataman´s group [9]. We subsequently found a way to reduce or even completely prevent analyte losses during the collection procedure: by using the stoichiometric excess of O_2 over H_2 in the quartz tube atomizer to effectively trap hydrides in the first (trapping) step of the collection procedure. This resulted in a very sensitive and practical methods for Sb, Bi, Se, As, Pb and Sn determination [10–18].

It has been postulated that most probably oxides of an analyte are formed in the trapping step of the collection procedure [10,11] with high affinity to the quartz surface. Subsequent volatilization of the trapped species in the second step of the collection procedure is realized by the change in the gas composition (decrease of O_2 flow and/or increase of H_2 introduced to the quartz tube atomizer). The range of volatile species suitable for this method was just recently extended to volatile species of Ag [19].

The disadvantage of the quartz tube atomizer lies in thermal durability of fused quartz (around 1100 °C) and susceptibility to devitrification at higher temperatures which is a slow process of rearranging from amorphous into crystalline structure (cristobalite) [20]. This devitrification is catalyzed by impurities, mainly alkali metals [21]. Water vapor and O_2 presence at increased temperature promote devitrification faster. Severe deterioration of the inner atomizer surface in the course of prolonged generation/atomization was recently observed in our laboratory in the case of volatile species generation of Ag [2,19,22], Au [3] and Pb [16] when high concentration of reagents (especially $NaBH_4$) was necessary for efficient generation. The co-generated fine aerosol containing also high amount of alkali metals and boron, and O_2 necessary for *in situ* collection (increasing further temperature by the reaction with H_2) are the main initiators of nucleation and subsequent growth of cristobalite. Such changes on the inner atomizer surface caused serious gradual signal broadening reflected in poor repeatability of the *in situ* collection signal shapes for Ag determination [19] given by changing volatilization rate from devitrified (roughened) surface of the optical tube. Very fast devitrification also substantially shortened the lifetime of the atomizer tube.

Very recently sapphire, which is an extremely pure alumina (5 N purity) in the form of corundum monocrystal [23], was proposed as a more suitable material of the optical tube resistant to devitrification or

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* Corresponding author.
E-mail address: stanomusil@biomed.cas.cz (S. Musil).

to other deterioration. The sapphire tube was successfully applied to atomize and to efficiently collect bismuthine in situ with similar analytical characteristics as a quartz tube. Since sapphire cannot be fused and easily connected to the other pieces, a modular atomizer design had to be used [24].

In this work sapphire was employed as a more resistant material of the atomizer optical tube for volatile species of Ag. The main task was to overcome the devitrification of the optical tubes and thus to substantially improve analytical performance of both on-line atomization and in situ collection mode.

2. Experimental

2.1. Instrumentation

An atomic absorption spectrometer Perkin-Elmer 503 with a Ag hollow cathode lamp (Perkin-Elmer, 328.1 nm, 0.7 nm spectral bandpass) operated at 12 mA without background correction was employed. Signals from the spectrometer´s output for a strip chart recorder were AD converted, collected and processed in a PC.

An Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) with liquid sampling was used to determine Ag contamination in reagents.

2.2. Standards and reagents

Deionized water (<0.2 μS cm^{-1}, Ultrapur, Watrex, Czech Republic) was employed for preparation of all solutions. Working Ag standards were prepared by serial dilution of 1000 μg ml^{-1} stock solution (Fluka, TraceCERT, Switzerland) in 0.6 M HNO$_3$ (semiconductor grade, Aldrich, Germany) that was also used as a carrier liquid. A reductant solution containing 2.4% (m/v) NaBH$_4$ (Acros Organics, Belgium) and 133 mg ml^{-1} of Antifoam B emulsion (Sigma, USA) in 0.1% (m/v) KOH (semiconductor grade, Sigma-Aldrich, Germany) was prepared fresh daily. 20 mg ml^{-1} of Triton X-100 (Aldrich Chemical Co., USA) in 0.1 M HNO$_3$ was used as a reaction modifier [25]. Standard reference material SRM 1643e by National Institute of Standards and Technology (NIST, USA) and two proficiency testing samples of drinking water SAR C from PT#V-9-2007 and PT#V-8-2008 tests produced by National Institute of Public Health (Prague, Czech Republic) with defined Ag contents were employed to verify accuracy of the analytical methods.

2.3. Generator

A generator of volatile species consisted of a chemifold with a mixing apparatus, gas–liquid separator (GLS) and spray chamber (Fig. 1). The reagents were pumped by a peristaltic pump 1 at the flow rate of 0.5 ml min^{-1}. Bubbles of H$_2$ evolving from NaBH$_4$ decomposition were removed from the reductant channel by means of a PTFE degassing chamber (0.5 ml) [26]. The sample was injected into a carrier liquid by a manual injection vent (with a 250 μl sample loop) and after on-line mixing with reaction modifier it reacted with the reductant in a special mixing apparatus. This mixing apparatus was in detail described elsewhere [2,26]. Briefly, it makes use of three capillaries of different inner diameters that are inserted in each other. These capillaries allow for mixing the sample with the reductant at the tip and at the same time disperse the reaction mixture to the whole glass GLS volume (3 ml) by means of carrier Ar. The waste liquid was pumped out at an arbitrary rate by a peristaltic pump 2 to maintain a stable level of the reacting mixture inside the GLS (approximately 0.5 ml). The clean mixing apparatus and GLS was pre-conditioned by means of volatile species generation from 4 ml of 10 mg ml^{-1} Pd solution (BDH, UK) in 0.1 M HNO$_3$ and 20 mg ml^{-1} Triton X-100 as described in detail in Ref. [27]. The outlet from the GLS was connected to a miniature double-pass spray chamber [2,25]. The flow rate of carrier Ar was 50 ml min^{-1} for all experiments. The flow rate of H$_2$ released from NaBH$_4$ decomposition in the GLS was measured as 26 ml min^{-1}. Where stated, an auxiliary flow of H$_2$ was introduced downstream the spray chamber via a T-piece to support the release of trapped Ag species. All gas flows were controlled by mass flow controllers (FMA-2400 or 2600 Series, Omega Engineering, USA).

2.4. Atomizer

A modular atomizer design was employed (Fig. 2) [19,24]. It comprised of: (i) inlet arm, (ii) outer body, (iii) optical tube placed inside the outer body, (iv) sealing and (v) cooling coils.

The inlet arm (100 mm long, 2 mm i.d., 4 mm o.d.) was made of sapphire (SapphiT® – Tempered Sapphire) and purchased from CRYTUR, spol. s.r.o. (Turnov, Czech Republic). It was connected via the T-piece serving for the introduction of auxiliary H$_2$ to the outlet from the spray chamber (see Fig. 1). The initial part of the inlet arm (~3.5 cm) was wrapped with the Ni80–Cr20 wire (~2.4 Ω total resistance, Omega Engineering, USA) for constant heating by laboratory power supply to 300 °C.

The outer body consisted of the outer quartz tube (165 mm long, 13.3 mm i.d., 16.3 mm o.d.) with two quartz inlets sealed to sides and one inlet sealed in the middle (see Fig. 2). Both side inlets served for introduction of outer O$_2$ to the cavity between the optical tube and the outer body. The central inlet of the outer body served as a mechanical support for the inlet arm.

The sapphire optical tube (SapphiT® – Tempered Sapphire) was used. It was 165 mm long with 7.1 mm i.d. and 11.0 mm o.d. and was purchased from CRYTUR, spol. s.r.o. (Turnov, Czech Republic). It had a central orifice (4.2 mm i.d.) that was by 0.2 mm broader than the outside diameter of the inlet arm (4 mm). The end of the inlet arm was aligned with the inner surface of the optical tube. As a consequence, there was a ring shaped slit, approximately 0.1 mm wide, that served
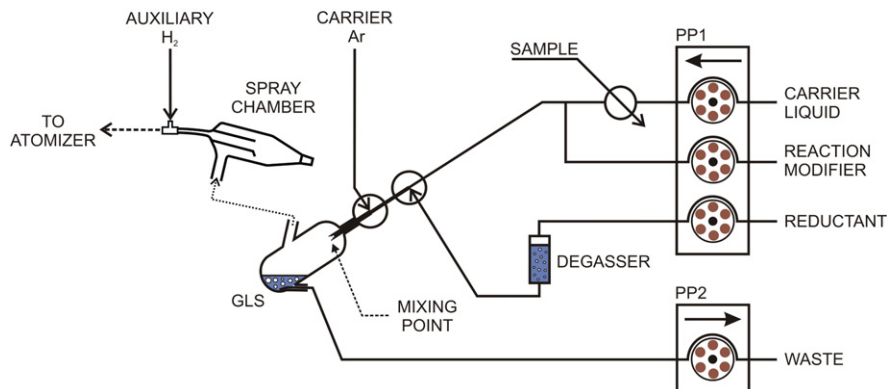

Fig. 1. Volatile species generator; PP1-2 – peristaltic pumps, GLS – gas–liquid separator.