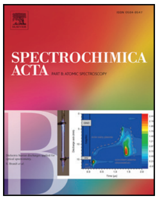
Spectrochimica Acta Part B 126 (2016) 11–16

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab



Studies on photochemical vapor generation of selenium with germicidal low power ultraviolet mercury lamp☆

B. Campanella [a,b], A. Menciassi [a], M. Onor [b], C. Ferrari [c], E. Bramanti [b], A. D'Ulivo [b,*]

[a] Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, 56124 Pisa, Italy
[b] C.N.R., Istituto di Chimica dei Composti Organometallici, S.S. di Pisa, Via Moruzzi, 1, 56124 Pisa, Italy
[c] C.N.R., Istituto Nazionale di Ottica, UOS di Pisa, Via Moruzzi, 1, 56124 Pisa, Italy

ARTICLE INFO

Article history:
Received 16 June 2016
Received in revised form 5 October 2016
Accepted 12 October 2016
Available online 14 October 2016

Keywords:
Photochemical vapor generation
Selenium
Formic acid
Germicidal lamp
Atomic fluorescence

ABSTRACT

Photochemical vapor generation (photo-CVG) with flow injection - atomic fluorescence spectrometry was investigated for the determination of selenium, using formic and acetic acids as photochemical reagents. Using a germicidal low power ultraviolet mercury-based lamp, emitting both the 185 and 254 nm Hg lines, mild reaction conditions can be achieved in formic acid medium, where optimal sensitivity was obtained at 0.3–0.5% w/w acid concentrations, whereas the optimal sensitivity could be attained with acetic acid in the range from 12 to 35% w/w. The only volatile Se product identified by gas chromatography–mass spectrometry from formic acid-based photo-CVG was selenium carbonyl. A series of dedicated experiments were performed using photo-CVG and pure dimethylselenide in order to identify reaction pathways contributing to the formation of non-volatile selenium species or to the degradation of volatile selenium species. Under the optimized conditions in formic acid, using 250 μL sample volume, the limits of detection and quantification were 0.10 and 0.35 μg L^{-1}, respectively. The effect of several interfering species was investigated and the method was tested in the analysis of certified reference materials.

1. Introduction

Chemical vapor generation (CVG) coupled with atomic and mass spectrometry represent a consolidated technique in analytical chemistry for the determination of many elements at trace and ultratrace level [1,2]. Today the chemistry and the mechanisms involved in this technique have reached a good degree of rationalization [3–5].

Thanks to the work of Sturgeon and coworkers [6–8] a CVG technique based on the use of ultraviolet radiation to promote the generation of volatile species, the photochemical vapor generation (photo-CVG), has opened the way for a new analytical technique for some of its favorable features over traditional CVG, which includes the elimination of borane complex reagents, strong inorganic acids and chemical additives, which are typically replaced by low molecular organic acids. Photo-CVG is mainly developing in the application field and suffers of a low degree of rationalization and only few papers deal with the discussion of fundamental aspects [6,9,10].

In this paper we report some selected results from our recent study on the photo-CVG of selenium (Se) using a flow injection (FI) generation system which includes a low power ultraviolet (UV) mercury lamps (emitting both the 185 and 254 nm Hg lines), coupled with a non-dispersive atomic fluorescence spectrometer (AFS). The aims of this work were to find mild reaction conditions, including low concentration of organic acids (formic and acetic acids) and to individuate some critical parameters which control the generation efficiency of volatile selenium compounds. The selected mild generation conditions for the photo-CVG procedure were tested for Se determination in certified reference materials.

2. Experimental

2.1. Instrumentation

2.1.1. Photo-CVG apparatus

A low-pressure mercury UV bench lamp (254 nm, 8 W, Hg-LC170, PureLab classic mk2, ELGA, UK), originally manufactured as an effective sterilization and sanitation instrument, was employed in combination with AFS detection.

Sample or blank were delivered to photo-CVG reactor with a high-pressure liquid chromatography (HPLC) gradient pump (P4000, ThermoQuest) equipped with a Rheodyne 7125 injector (Rheodyne, Cotati, CA) A 250 μL injection loop and sample flow rates of 3 mL min^{-1} were used. Under these conditions the residence time of the solution in the irradiated UV one was 25 s.

☆ Selected paper from the European Symposium on Atomic Spectrometry (ESAS 2016), Eger, Hungary, 31 March–2 April 2016.

* Corresponding author.
E-mail address: dulivo@pi.iccom.cnr.it (A. D'Ulivo).

http://dx.doi.org/10.1016/j.sab.2016.10.007

Selenium volatile compounds were generated in a flow-through UV-photoreactor consisting of a 2 m long FEP tube (0.8 mm i.d., total volume 1 mL) wrapped around the UV lamp.

The volatile selenium compounds generated were separated in a gas–liquid separator (borosilicate glass, 60 mm long, 10 mm i.d., inlet and outlet tubing 6 mm o.d. and 2 mm i.d.) by Ar/H_2 gas and the vapor coming out was delivered into the atomizer, which was a miniature Ar/H_2 diffusion flame (MDF) supported on a simple quartz tube (i.d. 4 mm). Because the photochemical reaction cannot produce excessive hydrogen, which together with argon is ignited to form an argon–hydrogen flame in the quartz atomizer of the AFS, for the atomization of the selenium volatile species hydrogen (120 mL min^{-1}) was added to the argon carrier gas. A peristaltic pump was used to pump off the waste liquid solutions. A schematic representation of the experimental set-up is reported in Fig. 1.

Selenium free atoms in the MDF atomizer were detected by a laboratory assembled non-dispersive atomic fluorescence (NDAF) detector equipped with an EDL Se lamp (Type II, Perkin Elmer, Monza, Italy) as the excitation source. The output data from the NDAF detector were collected with a personal computer equipped with a Dionex AI-450 chromatography interface and its acquisition software (Dionex PeakNet). A summary of experimental conditions is reported in Table 1.

2.1.2. CVG apparatus

In order to compare the sensitivity obtained by photo-CVG and CVG, the same apparatus as described in Section 2.1.1 was employed with the following modifications. The Se(IV) aqueous sample solution (250 μL,) was mixed on-line with 1 mol L^{-1} HCl (4 mL min^{-1}) and it was reduced with $NaBH_4$ solution (0.25 mol L^{-1} in 0.1 mol L^{-1} NaOH, 2 mL min^{-1}). The UV lamp was switched off and allowed to cool down to room temperature before starting CVG measurements.

2.1.3. GC–MS measurements

An Agilent 6850 gas chromatograph was used in combination with an Agilent 5975c mass spectrometer for the identification of selenium volatile products. The inlet liner was held at 200 °C and the injection was performed in splitless mode. Compounds were separated on a DB1-MS column (60 m × 0.25 mm, Agilent Technologies, Milan, Italy) using an isothermal at 30 °C with 1 mL min^{-1} helium flow. The temperature of the transfer-line was set at 280 °C. The MS acquisition was performed in total ion chromatography from 70 to 250 *m*/*z*.

Table 1
Experimental parameters for photo-CVG-AFS of Se(IV).

Selenium EDL	Lamp current	260 mA
	Modulation frequency	500 Hz
Sample flow rate		3 mL min^{-1}
Argon 1		160 mL min^{-1}
Argon 2		160 mL min^{-1}
Hydrogen		120 mL min^{-1}
Sample loop		250 μL

2.1.4. Spectrometric measurements

The intensities of the 185 and 254 Hg atomic lines emitted by the UV germicidal lamp were measured by an AvaSpec-2048-FT-SPU spectrometer (Avantes) set for a 170–439 nm spectral range. The spectrometer could be used in combination with a 0.5 m optical fiber (Avantes, FC-UV400-0.5-SR), which attenuates the 185 nm Hg line, but it can be usefully employed to evaluate relative intensity variation of the lines.

2.2. Reagents

The stock solution 1000 mg L^{-1} of selenite (H_2SeO_3 in HNO_3, Fluka AS standard solution) and pure dimethylselenide (>99%) were purchased from Sigma-Aldrich (Milan, Italy). Saturated aqueous solutions of dimethylselenide were employed for the investigation reported in Section 3.2.

Solutions of formic (HCOOH) and acetic acid (CH_3COOH) were prepared by appropriate dilution in deionized water of the respective concentrated reagents (HCOOH, ≥88.0% from Sigma-Aldrich, and CH_3COOH 99.9% from Carlo Erba, Italy).

Argon was used as the carrier gas and hydrogen was used as an auxiliary gas during the experiments (Rivoira, Italy).

Stock solution of 10% sodium borohydride ($NaBH_4$) in 1 mol L^{-1} sodium hydroxide (NaOH) were prepared from sodium tetrahydroborate salt (reagent for AAS, minimum assay > 96%, Merck & Co., Inc., N.J. USA) and 10 mol L^{-1} NaOH, obtained from dissolution in water of appropriate quantity of sodium hydroxide pellets (98%, Fluka Chemika, Sigma-Aldrich), and stored at 4 °C. All tetrahydroborate solutions were prepared daily by appropriate dilution of the stock solution.

Hydrochloric acid (HCl) diluted solutions were prepared from 37% (w/w) HCl (Carlo Erba, Rodano, Milan, Italy). Sulphuric acid diluted solutions were prepared using 95% sulphuric acid (ACS reagent, Sigma-Aldrich).

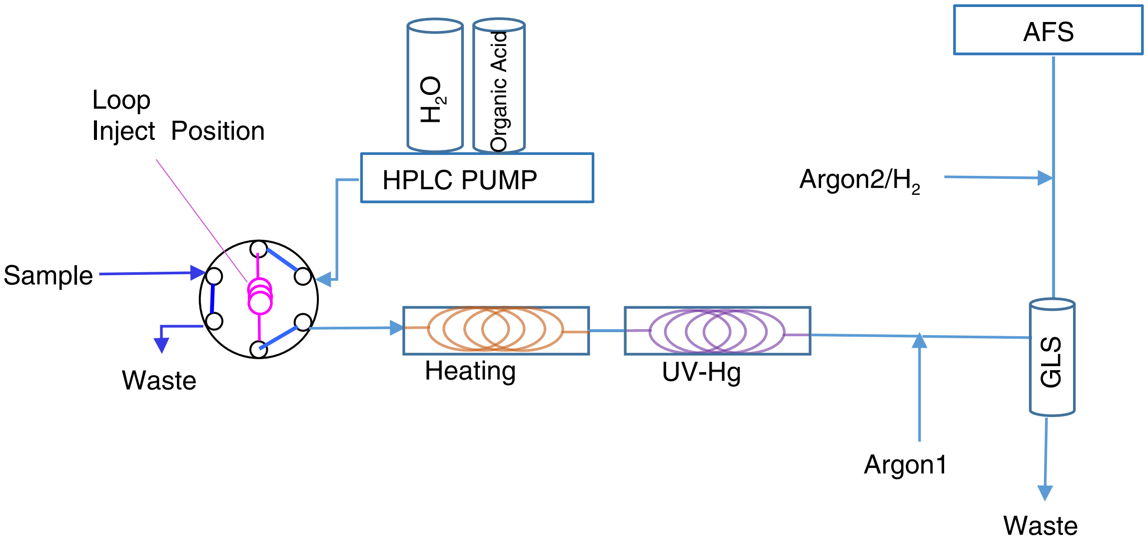


Fig. 1. Experimental set-up employed for Se photo-CVG.