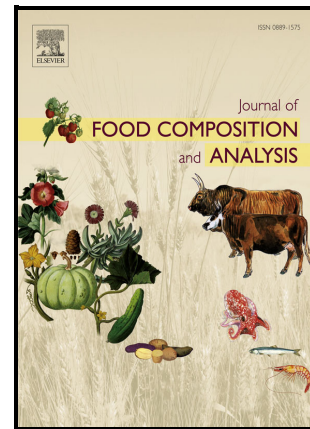# Journal Pre-proof

Sensitive method for total selenium determination in garlic and nuts by UV–photochemical vapor generation coupled to atomic absorption spectrometry using mild conditions

Jaime Palatnik, Agustín Londonio, Ezequiel Morzán, Rodolfo Wuilloud, Patricia Smichowski

Please cite this article as: Jaime Palatnik, Agustín Londonio, Ezequiel Morzán, Rodolfo Wuilloud and Patricia Smichowski, Sensitive method for total selenium determination in garlic and nuts by UV–photochemical vapor generation coupled to atomic absorption spectrometry using mild conditions, *Journal of Food Composition and Analysis,* (2023) doi:https://doi.org/10.1016/j.jfca.2023.105765

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Sensitive method for total selenium determination in garlic and nuts by UV–photochemical vapor generation coupled to atomic absorption spectrometry using mild conditions

Jaime Palatnik[a], Agustín Londonio[a,b], Ezequiel Morzán[a], Rodolfo Wuilloud[c,d], Patricia Smichowski[a,c],*

[a] Comisión Nacional de Energía Atómica, Gerencia Química, Av. Gral Paz 1499, 1650KNA–San Martín, Buenos Aires, Argentina.

[b] Instituto de Investigación e Ingeniería Ambiental (3iA), Universidad de San Martín, Martín de Irigoyen 3100, 1650–San Martín, Buenos Aires, Argentina.

[c] Consejo Nacional de Investigaciones Científicas y Técnicas, Av. Godoy Cruz 2290, C1425FQB, Buenos Aires, Argentina

[d] Laboratory of Analytical Chemistry for Research and Development (QUIANID), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Instituto Interdisciplinario de Ciencias Básicas (ICB), UNCUYO–CONICET, Padre J. Contreras 1300, 5500, Mendoza, Argentina

Corresponding author: P. Smichowski. E–mail: smichows@cnea.gov.ar; patricia.smichowski@gmail.com

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

1

CRediT authorship contribution statement

Jaime Palatnik: Conceptualization, Investigation, Methodology, Visualization, Validation, Writing – review & editing. **Agustin Londonio**: Conceptualization, Methodology, Writing – review & editing. **Ezequiel Morzan**: Software, Formal analysis. **Rodolfo Wuilloud**: Validation, Resources. **Patricia Smichowski**: Conceptualization, Writing – Original Draft, Writing – review & editing, Supervision.

ABSTRACT

Photochemical vapor generation (PVG) coupled on–line to atomic absorption spectrometry using a flow injection mode was investigated for the determination of total Se in garlic and nut samples. In the presence of low molecular weight organic acid solutions, Se(IV) is converted by UV irradiation to volatile species which are transported to the heated quartz tube atomizer. Formic and acetic acids were tested as photochemical reagents and a mixture of 1.5 % (v/v) formic and 5% (v/v) acetic acid was the best alternative. Central composite design was employed for parameters optimization. The effect of potential interfering elements such as hydride–forming elements, transition metals and nitric acid was investigated to ascertain possible effects of the matrix on Se(IV) signal. Under optimized

conditions a detection limit (LOD) of 33 ng g^{-1} (3σ) was reached. Samples of garlic and nuts purchased at a local market were analyzed and Se concentrations spanned the range 0.36 to 248 µg g^{-1}. These results were compared with ICP–MS measurements utilizing an elliptical joint confidence region (EJCR) with bilinear least squares analysis, and good results were obtained.

1. Introduction

Selenium is an essential trace element that is naturally present in different foods and added to others, and also Se is present in some dietary supplements. It is a constituent of more than two dozen selenoproteins that play critical roles in reproduction, thyroid hormone metabolism, DNA synthesis, and protection from oxidative damage and infection (Sunde, 2012). This metalloid is a very important and interesting trace element in terms of human biology and health being food the principal route of Se to enter the body. A special characteristic of Se is that it can be essential as well as toxic for humans having a narrow range between deficiency and toxicity (Dumont et al., 2006). This dual behavior and other characteristics have led to Se becoming a permanent topic of study. In this context, it is of prime importance to develop methodologies for its determination at the levels that Se can be found in food samples. As regard Se species in foodstuffs, selenomethionine (SeMet) is the

3

major species in food. It is found in cereals, grains, and soybeans. On the other hand, methylselenocysteine (MeSeCys) is mainly detected in Se–enriched garlic, onions, and wild leeks.

Chemical vapor generation (CVG) is a well–known, efficient and consolidated sample introduction technique for the determination of a variety of elements at trace and ultra–trace levels. Without any doubts, hydride generation (HG) based on the chemical reduction of the analyte with a reductant such as tetrahydroborate under acidic conditions is the most popular and well established CVG technique for trace elements of IV−VI main groups (e.g., As, Bi, Ge, Pb, Sb, Se, Sn, and Te), Hg, and Cd. The HG of a variety of transition metals was also reported (Marrero et al., 2002; Pohl et al., 2014; R. Sturgeon et al., 1996).

Nevertheless, in spite of the important advantages of HG for sample introduction, it is worth mentioning that solutions of NaBH$_4$ are quite unstable, and that the large amounts of hydrogen generated during HG process produces instability of the atomization source, especially when plasma sources are employed for detection. Interference associated to the presence of transition metals in the sample that by interaction with the NaBH$_4$ provoke its catalytic decomposition is another drawback to mention.

In the last years, greener sample preparation and introduction methods avoiding the use of corrosive and hazardous acids/reagents as well as high pressure and temperature have gained popularity. From the pioneering studies of Sturgeon and his group (Guo et al., 2003a, 2003b, 2003c), photochemical vapor generation (PVG), utilizing free radicals generated by a photo–redox reactions in the presence of low molecular weight organic acids has appeared as an interesting and powerful alternative to traditional chemical HG methods for sample introduction (R. E. Sturgeon, 2017; Yin et al., 2011).

For analytical purposes, this technique opened novel routes for introduction of chemical elements into atomic spectrometric sources. It was applied to generate volatile species of inorganic Se at room temperature using ultraviolet radiation (Guo et al., 2003c). PVG has extended in scope to a broader range of elements including nonmetals such as alkyl halide generation (Leonori et al., 2019). Briefly, in PVG the analyte is converted to a volatile species by the addition of a low molecular weight organic acid (photochemical agent) to the sample and subsequent exposure to the action of UV radiation. The generated volatile species are conducted on–line to the detection instrument in a flow of inert gas. In general, low–pressure Hg discharge lamps are used for irradiation of the media to induce PVG. Different acids have been tested as source of reducing radicals including, formic, acetic, malonic, and propionic (Guo et al., 2003c; Nováková et al., 2017).

In subsequent years, other authors reported the successful application of PVG to the determination of different elements/species in a diversity of matrices using different instrumental approaches. In the last 15 years, research on the generation of targeted volatile forms of As (Gao et al., 2015), Bi (Vyhnanovský et al., 2021), Hg (Covaci et al., 2017; Gao et al., 2010), Mo (Šoukal et al., 2018), Se (Campanella et al., 2016; da Luz Potes et al., 2019), Te (He et al., 2018) was developed to improve the detection power. In the case of Se, the presence of low molecular weight organic acids (formic, acetic, propionic, and malonic) leads to the conversion of inorganic Se(IV) through UV irradiation, resulting in the formation of volatile Se species such as carbonyl, dimethylselenide, and diethylselenide depending on the acid utilized. When formic acid is used as photochemical agent the volatile products of PVG are mainly SeH_2 and SeCO (carbonyl) in less proportion. In addition, when nitric acid is present in the reaction media the only volatile product identified was SeCO (Guo et al., 2003c).

The purpose of this study was to develop an optimized, sensitive, cost–effective and green method using optimized mild reaction conditions to generate volatile species of Se for its determination in different real food samples. Multivariate techniques were performed to determine the critical conditions of the experimental parameters.

2. Materials and methods

2.1. Instrumentation

All measurements were made using an atomic absorption spectrometer (AAS) PerkinElmer AAnalyst 200 provided with a quartz cell covered with an electrically heated mantle. A Se electrode less discharge lamp (PerkinElmer, Norwalk, CT, USA), was used as radiation source, operated with a current of 280 mA, at a resonance wavelength of 196.03 nm, and a slit width of 2.3 nm.

A schematic diagram of the instrumental set–up for the UV–PVG–AAS system employed in continuous on–line mode is shown in Fig. 1. In detail, a HPLC quaternary gradient pump Jasco model PU–2089 (Jasco, Easton, MD, USA) and a syringe injection six–port valve (Model 7725i, Rheodyne) with a 200 μL loop were used to inject and propel samples/reagents/blanks into the stream of the reaction medium at a flow rate of 5.0 mL min^{-1}. The photoreactor (PR) consists of 3.4 m long polytetrafluoroethylene (PTFE) tube (i.d. 1.0 mm / o.d. 1.5 mm, JQ Industries, Argentina) wrapped around a germicide low-pressure Hg vapor UV lamp (254 nm, 15 W, dimension 450 mm, Phillips). The PVG reactor was covered by wrapping it with aluminum foil to prevent operators from UV radiation and also served

to increase the efficiency by reflecting UV radiation. Argon with a purity of 99.999% from Air Liquid (Buenos Aires, Argentina) was used as carrier gas. It was introduced to the system through a "T" connection inserted between the outlet of the PR and the borosilicate gas liquid–separator (GLS), (part number M055G003, PS Analytical, UK), internal volume of 10 mL. Argon flow rate was controlled on–line by a flow–meter (maximum flow: 250 mL min^{-1}). To facilitate Se atomization, the outlet of the GLS was mixed with a flow of H$_2$ (auxiliary gas) introduced in the transport line through a "T" connection between the GLS and the quartz cell. Hydrogen gas was generated by a Canberra Packard model 9100 Generator (Schwadorf, Austria). The volatile Se compounds generated were transported from the GLS to the atomic absorption apparatus through a PTFE tube. PTFE tubes of various inner diameters were used as connecting material in the system. For pre–reduction of Se(VI) the samples were heated on a hot plate (LabTech EH20B). An EthosUP (Milestone, Bergamo, Italy) microwave apparatus equipped with 15 Teflon–PFA vessels was used to digest food samples.

An ultrasonic bath (Testlab, Buenos Aires, Argentina) was used to extract the Se compounds from the samples (frequency: 40 kHz; power: 160 W).

An inductively coupled plasma single quadrupole mass spectrometer PerkinElmer model NexION 300X was used for Se determination in food samples for comparison purposes. The instrumental parameters adopted are summarized elsewhere (Londonio et al., 2019).

2.2. Reagents and chemicals

Deionized distilled water (DDW) produced by an Arium® Water Purification System (Sartorius, Goettingen, Germany) was used for the preparation of all solutions. All reagents were of analytical grade. Concentrated nitric acid (65 % w/w), hydrochloric acid (37 % w/w) and hydrogen peroxide 30 % (w/w) (Merck, Darmstadt, Germany) of analytical grade were used for sample treatment and/or preparation of the standards. Nitric acid was additionally purified in a sub–boiling distillation system, Distillacid BSB–939–IR (Berghof, Eningen, Germany).

A stock solution of sodium selenate (Na_2SeO_4 in HNO_3 from Merck) was used. Solutions of formic (HCOOH) and acetic acid (CH_3COOH) were employed after appropriate dilution in DDW of the respective concentrated reagents (HCOOH, ≥88.0% from Anedra, and CH_3COOH 99.9% from Biopack). Nitric acid, HCl and H_2O_2 were used in different steps of the analytical procedure, as extraction agents, for pre–reduction of Se(VI) and for microwave–assisted digestion of food samples.

Standard solutions of As(III), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Sb(III), Zn (II) of 1000 mg L^{-1} (Merck) were employed in the study of interferences. Diluted working solutions were prepared daily by serial dilutions of the 1000 mg L^{-1} standard solutions. All glassware and plastic bottles used were cleaned by rinsing with DDW, soaking with a 10 % (v/v) HNO_3 solution for 24 h and then rinsing several times with DDW. All samples and standards were stored in polyethylene bottles (50 mL) or Falcon® tubes.

2.3 Samples analyzed

A total of 16 samples (garlic and nuts) were analyzed:

(i)   4 samples of garlic (*Allium sativum L.*) purchased in a local market in Buenos Aires, Argentina (identified as G1–G4)

(ii)   4 samples of garlic enriched with Se (identified as GE1–GE4). Selenium enrichment experiments of garlic samples are described elsewhere (Pérez et al., 2018).

(iii)   4 samples of nuts (*Juglans regia*) purchased from a local market in the city of Buenos Aires, Argentina (identified as N1–N4).

(iv)   4 samples of Brazilian nuts (*Bertholletia excelsa*) purchased in a market in Belém, Pará, Brazil (identified as BN1–BN4)

2.4. Sample preparation

Garlic samples were lyophilized and homogenized using a freeze dryer (Virtis, New York, USA) Model 6 Lyophiliser 12 L. For nuts, firstly they were ground using a mortar and pestle. Subsequently were dried at 60ºC until constant weight. After this step, a 6775 Freezer Mill cryogenic grinder (New Jersey, USA) was employed.

The pre-reduction step was performed by adding to the dried sample or calibration standard, 300 µL of concentrated HCl; then 2.5 mL of DDW were incorporated into the flask and heated in a water bath (85–90°C) for 30 minutes.

Samples under study must be necessarily put in solution before presenting them to the analytical technique selected for analysis. Three procedures were used and compared:

- Procedure 1– For formic acid solubilization, aliquots of 50 mg of powdered food samples were weighed directly into polypropylene tubes and 5 mL of HCOOH were added. The mixture was placed in a thermostated (60 °C) ultrasound bath for two cycles of 30 min each. Then, solutions were centrifuged at 4200 rpm for five minutes.

An aliquot of 1 mL of the supernatant was transferred into 15 mL volumetric flasks, for the pre-reduction of Se(VI) to Se(IV) and finally brought to the mark. All experiments were carried out in triplicate

- Procedure 2: Microwave–assisted acid digestion was also implemented in the preparation of food samples. To this end, aliquot of 500 mg of each sample were weighted into the digestion vessel and a mixture of 8 mL HNO_3 (65% w/w) and 1 mL H_2O_2 (30 % w/w) were added. The MW digestion program used was as follows: temperature ramped to 220 °C for 25 min, maintained at 220°C for 20 min and finally cooled to room temperature. After cooling, the vessels were opened and the digested solutions were transferred to polypropylene vials and evaporated to almost dryness on a digestion block (90 °C) to eliminate nitric acid. Dried residues were subjected to the pre-reduction step and redissolved in water to a final volume of 15 mL. All experiments were carried out in triplicate.

- Procedure 3– Microwave–assisted acid digestion for Se determination by ICP–MS: Samples were prepared as described in Procedure 2, but after cooling the digested solutions were transferred to volumetric flasks and DDW was added to reach a final volume of 15 mL.

2. 5. Analytical procedure

The PVG of volatile species of Se was carried out using a flow injection mode system. Solutions of Se standards or digested samples were injected into a 200 µL sample loop through a six–port valve. Then, the solution loaded in the loop was injected into the carrier solution flowing at 5.0 mL min^{-1} and transported to the PR where they were UV–

irradiated. The irradiated solution was mixed with Ar (120 mL min^{-1}) using a T–shaped connector and transported to the GLS to separate the volatile Se species from the liquid phase. After the GLS, the vapor was mixed with H$_2$ (5 mL min^{-1}) and transported through the transfer line to the quartz cell. The generated volatile Se compounds were atomized in the AAS instrument. Signal peak area was used for quantification. The whole procedure took about 1.5 min. A diagram of the experimental system employed is depicted in Fig. 1. More details are given in the Instrumental section.

Table 1 summarizes all optimized experimental conditions employed in this study.

2. 6. Optimization of experimental chemical and physical variables

The effect of different parameters on the efficient generation of volatile Se species was assessed for achieving the best performance of the system. For all the experiments of the optimization step, a solution containing 100 μg L^{-1} of Se(IV) was used. All tests were carried out by triplicate.

PVG efficiency is highly dependent on the type and concentrations of the organic acid selected. In a first approach, variables affecting the PVG of Se were examined separately. The critical parameters influencing the PVG of Se investigated were: (*i*) concentration of photochemical reagent, (*ii*) Ar (carrier gas) and H$_2$ (auxiliary gas) flow rates, (*iii*) irradiation time, and (iv) temperature of the inlet solution.

2.6.1. Screening studies for the parameters optimization

Preliminary tests were performed to find favorable reaction conditions to generate volatile Se species using low concentrations of organic acids. Formic and acetic acids were

investigated. Both acids were tested in the range: acetic, 0–10 % and formic, 0–30 %; alone and mixed in different proportions

In this investigation, a HPLC pump was used to propel solutions to ensure a constant flow of the organic acids assessed by mixing three lines, containing water and the organic acid/acids. In addition, using a HPLC pump for flow–injection made possible to accurately change the composition of the mobile phase during the optimization process.

Sample flow rate is inversely equivalent to sample residence/irradiation time for a fixed reactor volume. However, the sample flow rate was initially adjusted by varying it from 1 to 5 mL min^{-1}, with the objective to obtain an appropriate peak for analytical purposes in terms of height, shape, and width.

For the selected sample flow rate value, the residence time of Se within the irradiation process was adjusted by modifying the length of the PTFE tube wrapped around the UV lamp, ranging from 1 to 6 meters (corresponding to irradiation times varying from 9.4 to 56.5 s).

Concentrations of gases were studied in the range: Ar, 20–220 mL min^{-1}, and H$_2$, 0–25 mL min^{-1}. Higher flow rates were not tested to avoid dilution effects that would cause a decrease in the analytical signal of Se. The temperature of the inlet solution was also tested in the range from 25 ℃ to 55 ℃.

A multivariate optimization technique was selected in this study as described in the following pages.

2.6.2. Multivariate optimization

Two experimental designs namely, Design 1 and Design 2 were tested:

- Experimental Design 1 consisted in the optimization of the volatile Se species generation, and its transport (from the GLS to the atomization cell). The four variables included in this design were (*i*) acetic acid concentration, (*ii*) formic acid concentration, (*iii*) reactor length, and (*iv*) temperature of the inlet solution. A four factor–central composite design (CCD) was employed for modeling the response surface.

- Experimental Design 2 consisted in the optimization of the flow rates of the two gases: (*i*) Ar, employed to transport volatile species of Se to the GLS, and (*ii*) H_2, used for reduction and transport of volatile species of Se to the atomization cell. Therefore, two factors and five levels full factorial design (FF) were selected requiring a total of 25 experiments.

2.7. Calibration

Two calibration methodologies were followed. Under optimized conditions, an external calibration curve was established within the concentration range from LOQ to 100 $\mu g\ L^{-1}$ of Se (IV) for the determination of Se in garlic samples. For the complexity of the matrix, a three–point method of standard addition was employed for the determination of Se in nuts to obviate any potential matrix interferences.

2.8. Limits of detection and reliability criteria

Instrumental limits of detection (LOD) and quantification (LOQ) were calculated as the concentration associated with three (LOD) and ten times (LOQ) the standard deviation

of 10 independent measurements of the procedural blank (3σ criterion), respectively. Blanks were subjected to the same procedure that the samples.

The linearity was checked by an external calibration curve that was made in the range 0–150 μg L^{-1}, which included blanks and standards at concentrations of 5, 10, 20, 40, 60, 80, 100, and 150 μg L^{-1} of Se(IV).

The results obtained from the optimized method were compared with the ICP–MS measurement, utilizing an elliptical joint confidence region (EJCR) with bilinear least squares analysis (González et al., 1999).

The accuracy of the proposed method and matrix effect (interference of the food sample in the analytical response) were verified using an analytical recovery test. Independent aliquots from selected previously analyzed selected powdered food samples were subsampled and fortified with Se. Two concentration levels of 10 and 20 μg L^{-1}, corresponding to 0.3 and 0.6 μg g^{-1} in the solid, respectively, were used for the spikes. Then, samples were then subject to MW-assisted digestion and analyzed using the optimized PVG-AAS method.

2.9. Interference study

Using the optimized working conditions, the effect of potentially coexisting ions on the determination of Se (IV) by UV–PVG–AAS was investigated. To this end, solutions containing 100 μg L^{-1} of Se and the foreign ion under study, at two different levels, were subjected to the analytical procedure. Variations over ±5% in the analytical signal of Se in the presence of potential interfering ions were taken as interference.

The effect of hydride forming elements and transition metals such as As(III), Co(II), Cu(II). Fe(III), Mn(II), Ni(II), Sb(III) and Zn(II) was studied. Nitric and HCl acids were also investigated to assess their effect on Se signal in the conditions of the experiment.

2.10. Photochemical vapor generation efficiency

The efficiency of the UV–PVG system was estimated by the ratio of the sensitivity between the developed PVG method and conventional HG–AAS using sodium tetrahydroborate as reductant and the recommended conditions indicated by the manufacturer (Table S1).

3. Results and discussion

3.1. Sample treatment and evaluation of sample digestion procedures

An adequate sample preparation is a key step when PVG–AAS is used for Se quantification. When Procedure 1 was applied to garlic samples, an analytical signal corresponding to a recovery of ~ 20% was obtained; respect to the signal obtained using MW-digestion and ICP-MS quantification. However, when the same samples (Procedure 1) were measured by ICP–MS, the recoveries were ~90–110%. Similar results were reported by Lopes et al. when formic acid was used as extractant (Lopes et al., 2016). According to Thiry et al. (Thiry et al., 2012) Se in food samples is present as selenocysteine and selenomethionine (SeMet). The lower recovery obtained for PVG–AAS compared to ICP–MS measurements could be attributed to the mild conditions used in PVG; it could happen that the amino acid molecules remain practically intact and that therefore the pre–reduction

step was not as efficient as expected. However, it is reported that Se(VI) may be present which is unreactive to PVG and that the direct PVG does occur for selenocysteine and selenomethionine (Suzuki et al., 2012). On the other hand, when Procedure 2 (MW digestion) was tested, recoveries better than 90% were obtained. In this case, after MW digestion, an evaporation step was also introduced to eliminate the HNO_3 used for digestion since the presence of NO_3^- produces severe interferences in the production of volatile species of Se (described in detail in *3.4, Interference Study* section).

3.2. Screening studies for the parameters optimization

Screening experiments showed that formic and acetic acids have a significant impact on Se response; the intensity of Se(IV) signal increased with the increased concentrations of both acids. The presence of acetic acid resulted in a less pronounced dependence of the signal on acid concentration.

It was observed that the mixture of both acids increased the efficiency facilitating the photochemical reduction of Se. In this context, a multivariate optimization was carried out as described in the next section.

The Ar carrier gas flow rate used to propel the sample through the transfer line to the GLS determines the liquid–gas separation efficiency of the volatile Se species. This gas also significantly influences the atomization of the analyte in the heated quartz cell. The addition of a stream of H_2 is necessary to achieve an effective atomization; it is due to the generation of free radicals necessary to atomize SeH_2. A rapid removal is advantageous to avoid decomposition of the generated species. Both gases produced a significant impact on Se signal.

The Teflon transfer line between the GLS and the quartz tube was kept as short as possible (about 30 cm). However, no significant differences were observed at greater lengths (up to 75 cm). This fact is in concordance with that reported by Guo et al., who reported that once formed the volatile species of Se they are very stable and does not suffer any losses during the transport process (Guo et al.; 2003).

3.3. Multivariate optimization

The response surface was fitted to the Experimental data of Designs 1 and 2, leading to the determination of optimized parameters for Se(IV) using PVG-AAS.

3.3.1. Experimental Design 1

The response surface fitted for Experimental Design 1 is shown in Figs 2a and 2b and the equation obtained is included in Supplementary Information. The best fitting model was quadratic polynomial.

The evaluation of model fitness was evaluated by ANOVA test described by Bezerra et al. (Bezerra et al., 2008), and the model fitness obtained can be considered satisfactory. Furthermore, to show its fitness actual measured value *vs* value predicted by the model was plotted and shown in Fig 2c. The figure shows that the points are in a straight line of slope ~ 1 and intercept ~ 0.

The model shows that temperature has no significant contribution to Se (IV) signal, at least in the range studied. These results agree with those reported by Guo et al. (Guo et al., 2003b). The optimal parameters were: acetic acid concentration: 5% (v/v); formic acid concentration: 1.5 % (v/v); reaction coil length: 3.4 m (equivalent to an irradiation time of 32 s) and temperature of the inlet solution: 20–25 ºC.

3.3.2. Experimental Design 2

The response surface fitted for Experimental Design 2 obtained is shown in Fig 3a and the equation obtained is included in Supplementary Information. The best fitting model was cubic polynomial.

The evaluation of model fitness evaluated by ANOVA test and the model fitness obtained can be considered satisfactory. Furthermore, to show its fitness, actual measured value *vs* values predicted by the model were plotted and shown in Fig 3b, The points of the curve are in a straight line with a slope ~ 1 and intercept ~ 0.

The optimal parameters found for the system under study were: Ar: 120 mL min^{-1}; H$_2$: 5 mL min^{-1}.

Factors and levels used in the factorial design are depicted in Table S2.

3.4. PVG Interference study

It is well known that the determination of Se by HG technique is seriously affected by the presence of transition metals, mainly Co, Cu, and Ni. Additionally, potential interferences arise from hydride–forming elements, which can lead to gas–phase interference in the heated quartz tube. The results of the interference study are presented in Table 2.

Respect to the hydride forming elements tested, the presence of As and Sb did not produce interference in the determination of Se by PVG–AAS as it occurs when HG is used.

Copper is a typical transition metal that can produce depression on Se signal at concentrations higher than 1.0 mg L^{-1}. According to Campanella et al. (Campanella et al., 2016) the depressing effect could be ascribed to the formation of metallic Cu(0), producing

a heterophasic system in the reaction coil. Rybínová et al. (Rybínová et al., 2016) also reported that Cu(II) was the most interfering transition metal affecting seriously the determination of Se by PVG. In our study, Cu depressed severely Se signal as follows: – 37% and –57% when 1.0 mg L^{-1} and 10 mg L^{-1} Cu were added to the test solutions, respectively. No significant interference from Co, Fe, Mn, Ni, Co and Zn was detected when 1.0 mg L^{-1} were present in the Se containing sample solution. On the other hand, when concentrations of 10 mg L^{-1} were tested, Se signal was reduced. It is important to note that concentrations of Fe, Mn and Ni of 10 mg L^{-1} are not levels expected in the samples analyzed in this study.

      Positive interferences were also reported in the literature. In this direction, other authors added transition metals at trace levels as sensitizers/catalysts for PVG. They include metals such as Ni(II), Cu(II), and Cd(II) to increase the production of volatile species of Pb, Co, As, Cl, Se and Te when generated in solutions of UV–irradiated acetic and formic acids (Leonori et al., 2019). This behavior was used by Xu et al. (Xu et al., 2018) to enhance the in situ production of Se(VI) by adding Cd(II) to an acetic acid reaction medium forming a nano–CdSe photocatalyst. In our study, no significant enhancing effects were observed for the elements tested.

      There is another group of concomitants that deserves to be studied. Nitric and hydrochloric acids are common concomitant since they are frequently used for sample digestion. According to our screening experiments, the presence of both acids produced an increase in the generation efficiency of Se volatile compounds. Leonori & Sturgeon (Leonori et al., 2019) postulated mechanisms involving redox termination of radical chain reactions, especially from oxidants such as dissolved O_2, NO_3^- and NO_2^-; being nitrite interference more severe. In addition, they reported that Se signal intensity increases in the same way by

19

the presence of NO_3^- or NO_2^- anion deriving from either sodium nitrate or sodium nitrite. According to Mollo and Knochen (Mollo et al., 2020) nitrate, reacts with the reductant radicals decreasing its availability and yielding oxidizing species. When this occurs, the medium is no longer reductant and the formation of the volatile species is quenched. Several authors investigated the adverse effects caused by NO_3^- as well as the different methods used for the abatement of nitrate interference (Lopes et al., 2016; Mollo et al., 2020).

Figure S1a shows the dependence of Se absorbance when HNO_3 was tested indicating that the nitric acid has a marked influence on the Se signal. Our results are in good agreement with those reported by Rybinova et al (Rybínová et al., 2016). In Fig S1b, similar results were obtained when HCl was assessed. Consequently, in our study, in the MW–assisted digestion of real samples, the amount of oxidizing acids was minimized and digested samples were evaporated to almost dryness and re-solubilized in diluted HCl.

3.5. Analytical performance

Using optimized analytical conditions, the obtained values of LOD and LOQ were 1.1 µg L^{-1} and 3.6 µg L^{-1}, which correspond to 33 ng g^{-1} and 109 ng g^{-1} in the solid, respectively. For comparative purposes, our results were compared in Table S3 (supplementary information) with those reported in the literature. In general terms, our results are of the same order of magnitude that those reported previously, except those reported by Rybínová and coworkers (Rybínová et al., 2016).

Linearity was attained from levels close to the LOQ up to 100 μg L^{-1}. The repeatability expressed as the relative standard deviation (% RSD, n = 10) was 2% at a Se(IV) level of 100 μg L^{-1}.

The coefficient of determination (R^2) of the calibration curve was better than 0.997 until Se(IV) concentration exceeded 100 μg L^{-1}. From this value R^2 began to decline. This effect could be attributed to the fact that at higher Se (IV) concentrations the efficiency of generation is lower.

The comparison of results from the PVG–AAS optimized method with the ICP–MS measurement is shown in Fig. S2a. The optimized method is as accurate as the ICP–MS method, as depicted in Fig. S2b, due to the ideal point (coordinates: a=0, b=1) is inside the EJCR.

Recoveries in the garlic samples analyzed varied between 93 and 107%. Results of the recovery test are depicted in Table 3.

3.6. Photochemical vapor generation efficiency

The efficiency of the PVG is the fraction of the analyte Se (IV) that can be removed from solution and determined in the whole process. The sensitivity values of the optimized PVG method and conventional HG–AAS were 0.0132 L μg $^{-1}$ and 0.0292 L μg^{-1}, respectively. These values were used to calculate the efficiency. In both analytical techniques, the efficiency depends on a series of parameters namely, vapor generation; separation of the volatile analyte in GLS from condensed phase; and transportation from GLS to the AAS instrument. For calculation, we assumed that conventional CVG–AAS has efficiency of 100% efficiency. The efficiency achieved in this study was 46%, which is comparable to the value reported by Guo et al. of $50 \pm 10\%$ using acetic and malonic acids, and significantly higher than the reported efficiency of 10–15% when formic acid was used alone (Guo et al., 2003c). Nevertheless, this value was lower than the 79% efficiency reported

by da Luz Potes *et al*, 2019, who employed PVG coupled to graphite furnace atomic absorption spectrometry (GF–AAS) (da Luz Potes *et al*., 2019). The disparity in efficiency may be attributed to the fact that the quartz PR exhibits much higher UV–C transmission compared to the PTFE tubing employed in our study. Nevertheless, PTFE tubing has the advantage of its flexibility and durability.

3.7. Analysis of real samples

Data concerning Se determination in food samples is scarce. In our opinion, it can be attributed to the complexity of methods used for Se detection and quantification in food at trace and ultra–trace levels. Recently, da Silva et al reported an illustrative study on the accumulation and localization of Se and Ba in nuts using spectroanalytical techniques (da Silva Junior et al., 2022). In another study, the accumulation of Se in plant foods and Se intake of residents in a moderately Se-enriched area was described (Li et al., 2023).

Although PVG has been used for some analytes determination as described before, matrix effects and sample preparation remain a challenge for this technique when applied to the analysis of real samples. For this reason, it can be observed in the literature that published studies generally analyze liquid samples and only a minority part of the studies analyze solid samples.

For comparative purposes, samples under study were also determined by ICP–MS after MW–sample digestion (Table 4). Determination of Se by ICP–MS is in general a difficult task because it is hampered by spectral interferences. It is affected by the presence of polyatomic ions, such as $^{40}Ar_2^+$ or $^{12}C^{35}Cl_2^+$, and the effects of these ions may be overcome by using different strategies, such as *(i)* the selection of another isotope, *(ii)* the use of

22

mathematical correction, *(iii)* the use of cool plasma or *(iv)* the use of reactions and/or collisions by the introduction of a variety of gases. Strategy *(i)* was selected in this study, and the ^{82}Se isotope, which is free from the Ar-Ar interference, was chosen. However, its low natural abundance of 8.73% yields a poor LOD. To solve this problem, a 3% v/v methanol (final concentration) was added to the sample and standards to enhance the signal (Sullivan et al., 2013). Concentrations of Se (expressed in µg g^{-1}) in garlic and nuts samples are shown in Table 4. Results were compared with those obtained by ICP-MS and percentage errors were calculated.

4. Conclusions

On the basis of the outcome of this study, it can be concluded that PVG of Se(IV) using FI–AAS and a low power UV Hg lamp can be achieved using mild conditions with a mixture of 1.5 % (v/v) formic and 5% (v/v) acetic acid as photochemical reagents. No additional chemicals were essentially needed to generate volatile Se compounds and the interface is simple and can be adopted as alternative for rapid and friendly determination of other elements. In comparison with conventional HG methods, tetrahydroborate is avoided and therefore the generation of hazardous substances is reduced or eliminated. In addition, concentrated HCl is not necessary for volatile species generation.

Optimization of the different variables involved in the PVG process was performed using chemometric tools that allowed mapping the entire experimental domain studied.

Data obtained for the analysis of real solid samples show that UV–PVG could become an alternative route of volatile compounds generation due to its relatively low cost,

simplicity, high sensitivity and green profile. In addition, the necessary instrumentation is easy to find in any analytical laboratory.

Our future PVG studies will be focused to study the use of photocatalysts, including nanomaterials, to improve the conversion efficiency of elements for achieving higher sensitivities.

Supplementary

Fig. S1. a) Effect of HNO$_3$ concentration on analytical response for 100 μg L^{-1} of Se(IV); b) Effect of HCl concentration on analytical response for 100 μg L^{-1} of Se(IV)

Fig. S2. a) Comparison of PVG-AAS vs. ICP-MS measurements; b) Elliptical joint confidence region for the regression slope and intercept of PVG-AAS vs ICP-MS measurements.

References

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta, 76*(5), 965-977. https://doi.org/10.1016/j.talanta.2008.05.019.

Campanella, B., Menciassi, A., Onor, M., Ferrari, C., Bramanti, E., & D'Ulivo, A. (2016). Studies on photochemical vapor generation of selenium with germicidal low power ultraviolet mercury lamp. *Spectrochimica Acta Part B: Atomic Spectroscopy, 126*, 11-16. https://doi.org/10.1016/j.sab.2016.10.007.

Covaci, E., Senila, M., Ponta, M., Darvasi, E., Petreus, D., Frentiu, M., & Frentiu, T. (2017). Methylmercury determination in seafood by photochemical vapor generation capacitively coupled plasma microtorch optical emission spectrometry. *Talanta, 170*, 464-472. https://doi.org/10.1016/j.talanta.2017.04.036.

da Luz Potes, M., Nakadi, F. V., Frois, C. F. G., Vale, M. G. R., & da Silva, M. M. (2019). Investigation of the conditions for selenium determination by photochemical vapor generation coupled to graphite furnace atomic absorption spectrometry. *Microchemical Journal, 147*, 324-332. https://doi.org/10.1016/j.microc.2019.03.053.

da Silva Junior, E. C., Duran, N. M., de Lima Lessa, J. H., Ribeiro, P. G., de Oliveira Wadt, L. H., da Silva, K. E., . . . de Oliveira Junior, R. C. (2022). Unraveling the accumulation and localization of selenium and barium in Brazil nuts using spectroanalytical techniques. *Journal of Food Composition and Analysis, 106*, 104329.

Dumont, E., Vanhaecke, F., & Cornelis, R. (2006). Selenium speciation from food source to metabolites: a critical review. *Analytical and bioanalytical chemistry, 385*, 1304-1323. https://doi.org/10.1007/s00216-006-0529-8.

Gao, Y., Sturgeon, R. E., Mester, Z., Hou, X., & Yanga, L. (2015). Multivariate optimization of photochemical vapor generation for direct determination of arsenic in seawater by inductively coupled plasma mass spectrometry. *Analytica Chimica Acta, 901*, 34-40. https://doi.org/https://doi.org/10.1016/j.aca.2015.10.020.

Gao, Y., Yang, W., Zheng, C., Hou, X., & Wu, L. (2010). On-line preconcentration and in situ photochemical vapor generation in coiled reactor for speciation analysis of mercury and methylmercury by atomic fluorescence spectrometry. *Journal of Analytical Atomic Spectrometry, 26*(1), 126-132. https://doi.org/10.1039/C0JA00137F.

González, A. G., Herrador, M. A., & Asuero, A. n. G. (1999). Intra-laboratory testing of method accuracy from recovery assays. *Talanta, 48*(3), 729-736. https://doi.org/10.1016/S0039-9140(98)00271-9.

Guo, X., Sturgeon, R. E., Mester, Z., & Gardner, G. J. (2003a). Photochemical alkylation of inorganic selenium in the presence of low molecular weight organic acids. *Environmental Science & Technology, 37*(24), 5645-5650. https://doi.org/0.1021/es034418j.

Guo, X., Sturgeon, R. E., Mester, Z., & Gardner, G. J. (2003b). UV light-mediated alkylation of inorganic selenium. *Applied Organometallic Chemistry, 17*, 575-579. https://doi.org/10.1002/aoc.473.

Guo, X., Sturgeon, R. E., Mester, Z., & Gardner, G. J. (2003c). UV Vapor Generation for Determination of Selenium by Heated Quartz Tube Atomic Absorption Spectrometry. *Analytical Chemistry, 75*, 2092–2099. https://doi.org/10.1021/ac020695h.

He, H., Peng, X., Yu, Y., Shi, Z., Xu, M., Ni, S., & Gao, Y. (2018). Photochemical vapor generation of tellurium: synergistic effect from ferric ion and nano-TiO2. *Analytical Chemistry, 90*(9), 5737-5743. https://doi.org/10.1021/acs.analchem.8b00022.

Leonori, D., & Sturgeon, R. E. (2019). A unified approach to mechanistic aspects of photochemical vapor generation. *Journal of Analytical Atomic Spectrometry, 34*(4), 636-654. https://doi.org/10.1039/C8JA00354H.

Li, X., Luo, Y., Zeng, C., Zhong, Q., Xiao, Z., Mao, X., & Cao, F. (2023). Selenium accumulation in plant foods and selenium intake of residents in a moderately selenium-enriched area of Mingyueshan, Yichun, China. *Journal of Food Composition and Analysis, 116*, 105089. https://doi.org/https://doi.org/10.3389%2Ffnut.2022.962312.

Londonio, A., Morzán, E., & Smichowski, P. (2019). Determination of toxic and potentially toxic elements in rice and rice-based products by inductively coupled plasma-mass spectrometry. *Food chemistry, 284*, 149-154. https://doi.org/10.1016/j.foodchem.2019.01.104.

Lopes, G. S., Silva, F. L., Grinberg, P., & Sturgeon, R. E. (2016). An evaluation of the use of formic acid for extraction of trace elements from Brazil nut and babassu coconut and its suitability for multi-element determination by ICP-MS. *Journal of the Brazilian Chemical Society, 27*, 1229-1235. https://doi.org/10.5935/0103-5053.20160018

Marrero, J., & Smichowski, P. (2002). Evaluation of vapor generation for the determination of nickel by inductively coupled plasma-atomic emission spectrometry. *Analytical and bioanalytical chemistry, 374*, 196-202. https://doi.org/10.1007/s00216-002-1372-1.

Mollo, A., & Knochen, M. (2020). Towards the abatement of nitrate interference on selenium determination by photochemical vapor generation. *Spectrochimica Acta Part B: Atomic Spectroscopy, 169*, 105875. https://doi.org/10.1016/j.sab.2020.105875.

Nováková, E., Linhart, O., Červený, V., Rychlovský, P., & Hraníček, J. (2017). Flow injection determination of Se in dietary supplements using TiO2 mediated UV-photochemical volatile species generation. *Spectrochimica Acta Part B: Atomic Spectroscopy, 134*, 98-104. https://doi.org/10.1016/j.sab.2017.06.007.

Pérez, M. B., Maniero, M. Á., Londonio, A., Smichowski, P., & Wuilloud, R. G. (2018). Effects of common cooking heat treatments on selenium content and speciation in garlic. *Journal of Food Composition and Analysis, 70*, 54-62. https://doi.org/10.1016/j.jfca.2018.04.004.

Pohl, P., Jamroz, P., Welna, M., Szymczycha-Madeja, A., & Greda, K. (2014). Chemical-vapor generation of transition metals through the reaction with tetrahydroborate in recent achievements in analytical atomic spectrometry. *TrAC Trends in Analytical Chemistry, 59*, 144-155. https://doi.org/10.1016/j.trac.2014.04.010.

Rybínová, M., Červený, V., Hraníček, J., & Rychlovský, P. (2016). UV-photochemical vapor generation with quartz furnace atomic absorption spectrometry for simple and sensitive determination of selenium in dietary supplements. *Michrochemical Journal, 124*, 584-594. https://doi.org/10.1016/j.microc.2015.10.004.

Šoukal, J., Sturgeon, R. E., & Musil, S. (2018). Efficient Photochemical Vapor Generation of Molybdenum for ICPMS Detection. *Analytical Chemistry, 90*(19), 11688–11695. https://doi.org/10.1021/acs.analchem.8b03354.

Sturgeon, R., Liu, J., Boyko, V., & Luong, V. (1996). Determination of copper in environmental matrices following vapor generation. *Analytical Chemistry, 68*(11), 1883-1887. https://doi.org/10.1021/ac951259g.

Sturgeon, R. E. (2017). Photochemical vapor generation: a radical approach to analyte introduction for atomic spectrometry. *Journal of Analytical Atomic Spectrometry, 32*, 2319-2340. https://doi.org/10.1039/C7JA00285H.

Sullivan, D., Zywicki, R., & Yancey, M. (2013). Method for the determination of total selenium in a wide variety of foods using inductively coupled plasma/mass spectrometry. *Journal of AOAC International, 96*(4), 786-794. https://doi.org/10.5740/jaoacint.12-389.

Sunde, R. (2012). Selenium. In A. C. Ross, B. Caballero, R. J. Cousins & K. L. Tucker (Eds.), *Modern nutrition in health and disease*. Philadelphia, PA: Lippincott Williams & Wilkins: Jones & Bartlett Learning.

Suzuki, T., Sturgeon, R. E., Zheng, C., Hioki, A., Nakazato, T., & Tao, H. (2012). Influence of speciation on the response from selenium to UV-photochemical vapor generation. *Analytical sciences, 28*(8), 807-811. https://doi.org/https://doi.org/10.2116/analsci.28.807.

Thiry, C., Ruttens, A., De Temmerman, L., Schneider, Y.-J., & Pussemier, L. (2012). Current knowledge in species-related bioavailability of selenium in food. *Food chemistry, 130*(4), 767-784. https://doi.org/10.1016/j.foodchem.2011.07.102.

Vyhnanovský, J., Yildiz, D., Štádlerová, B., & Musil, S. (2021). Efficient photochemical vapor generation of bismuth using a coiled Teflon reactor: Effect of metal sensitizers and analytical

performance with flame-in-gas-shield atomizer and atomic fluorescence spectrometry. *Microchemical Journal, 164*, 105997. https://doi.org/10.1016/j.microc.2021.105997.

Xu, F., Zou, Z., He, J., Li, M., Xu, K., & Hou, X. (2018). In situ formation of nano-CdSe as a photocatalyst: cadmium ion-enhanced photochemical vapour generation directly from Se (VI). *Chemical Communications, 54*(38), 4874-4877. https://doi.org/10.1039/C8CC01513A.

Yin, Y., Liu, J.-F., & Jiang, G. (2011). Photo-induced chemical-vapor generation for sample introduction in atomic spectrometry. *Trends in Analytical Chemistry, 30*(10), 1672-1684. https://doi.org/10.1016/j.trac.2011.04.021.
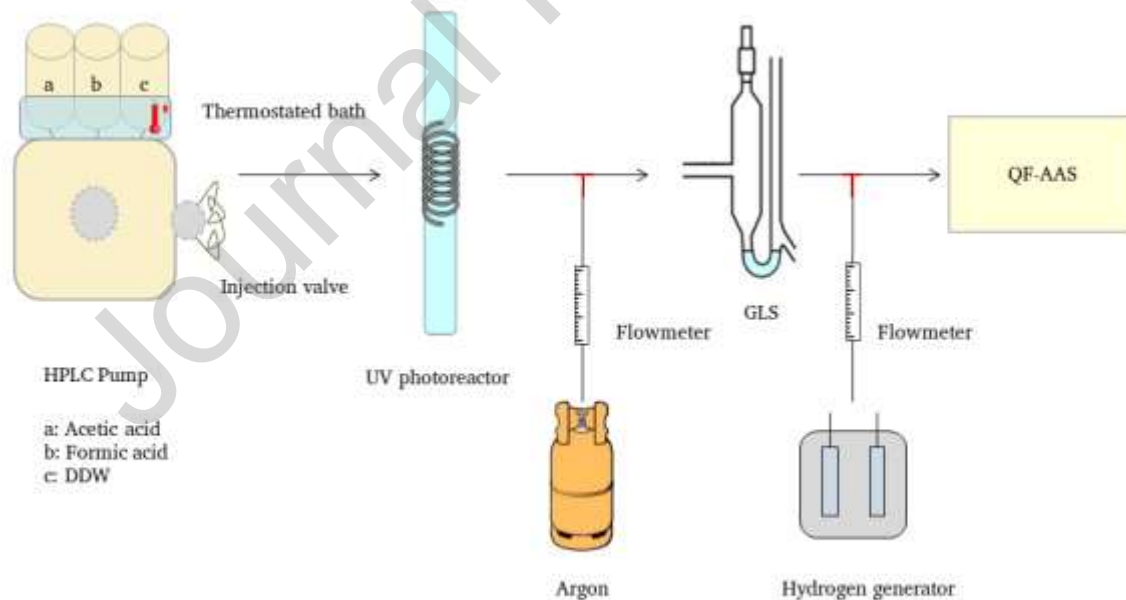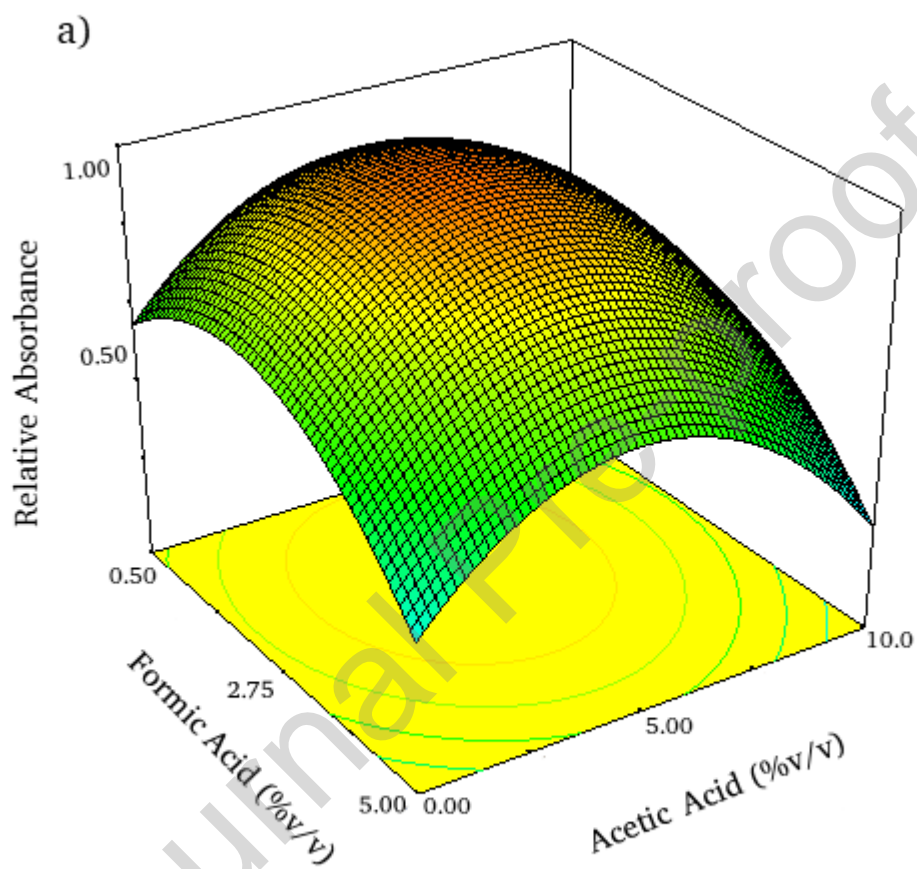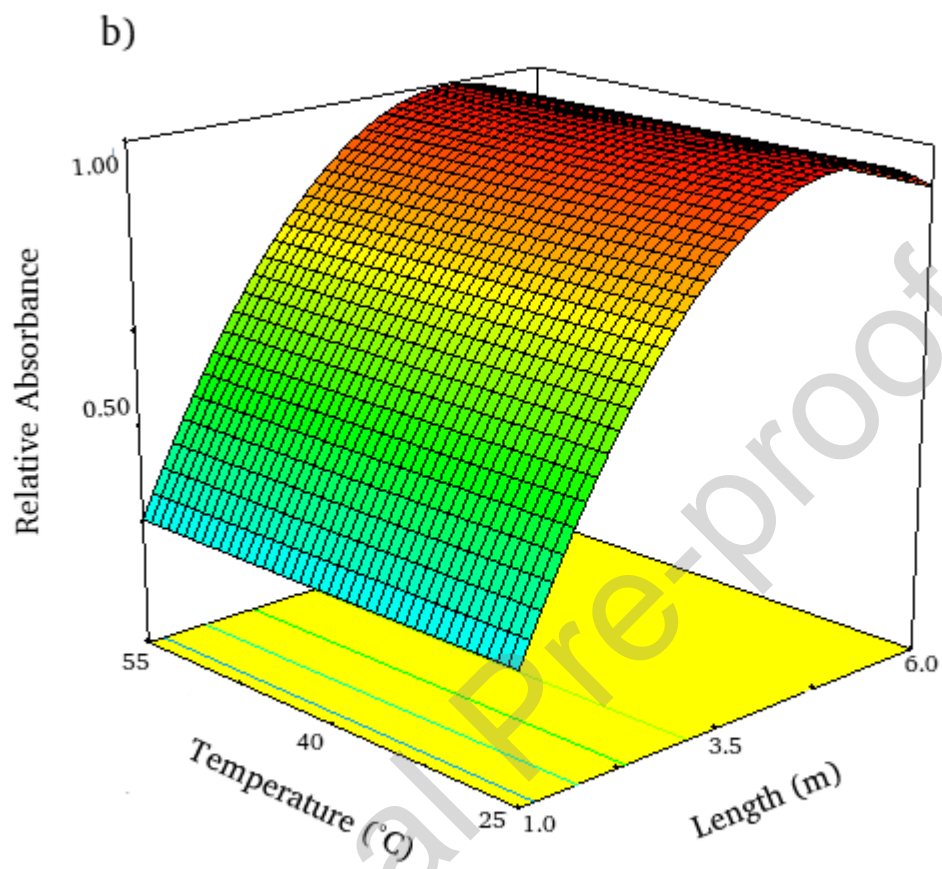
FIGURE CAPTIONS

Fig. 1. Schematic diagram of the instrumental set-up for the UV-PVG-AAS system employed in continuous on-line mode
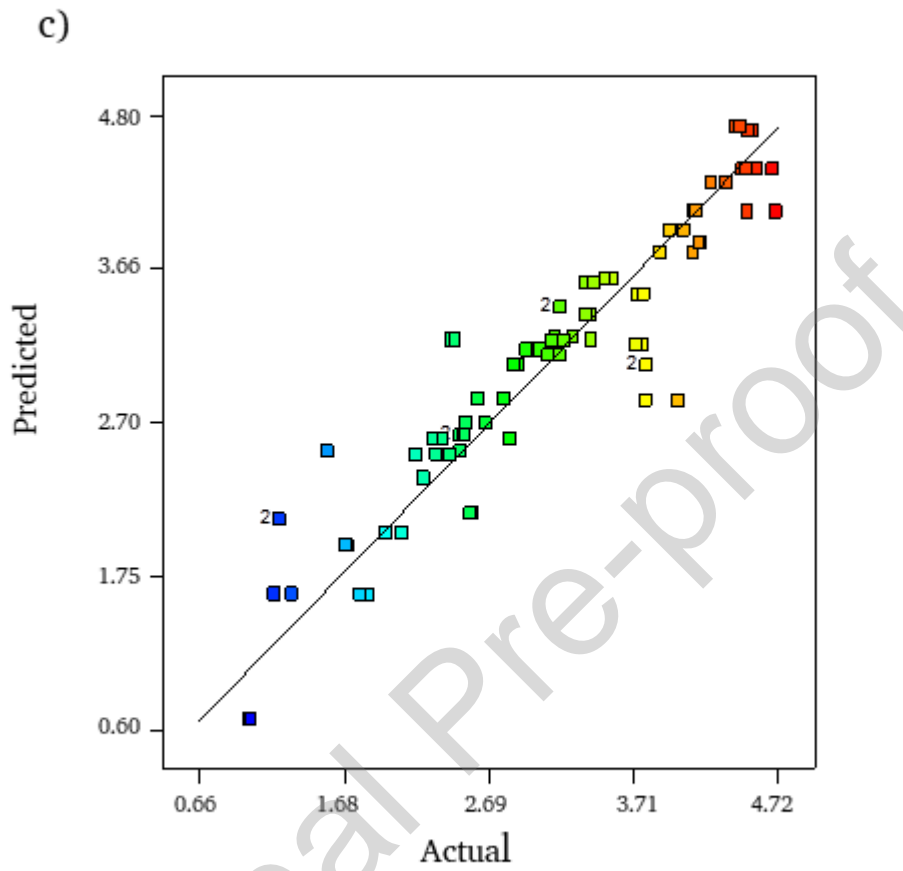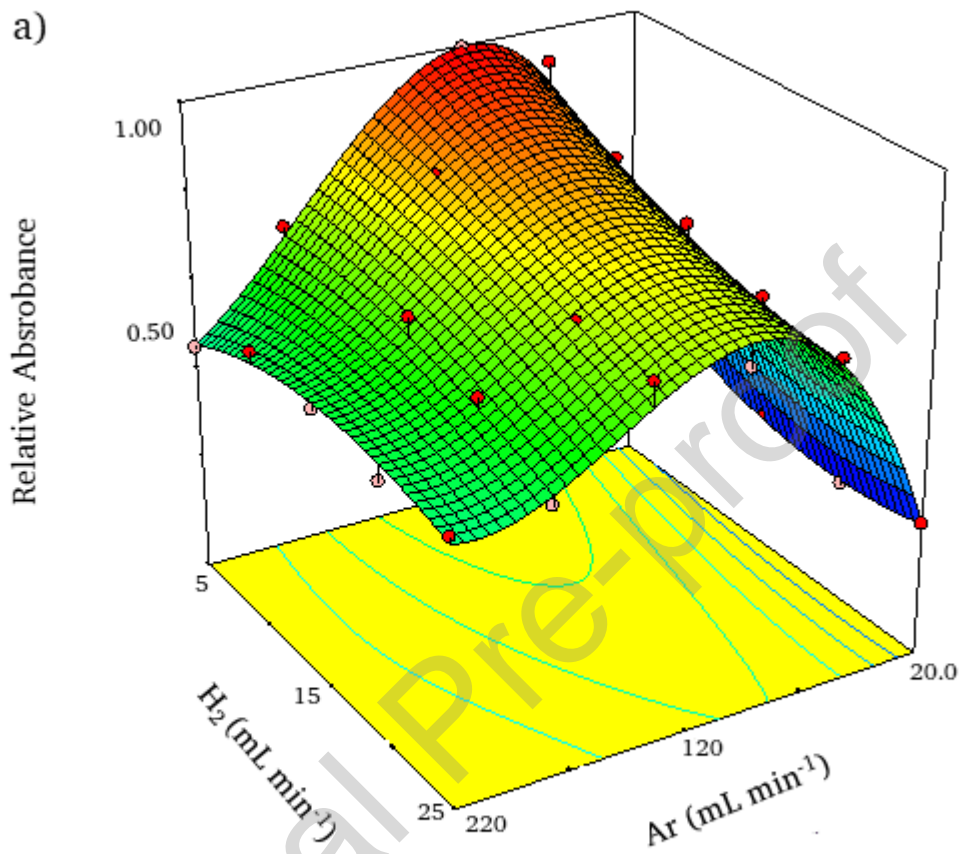
b)

Fig. 2. Empirical response surface fitted for Design 1 with quadratic polynomic: a) 3D visualization of fitted surface for acetic acid and formic acid; b) 3D visualization of fitted temperature and reactor length; c) area predicted by the model vs actual measured value.
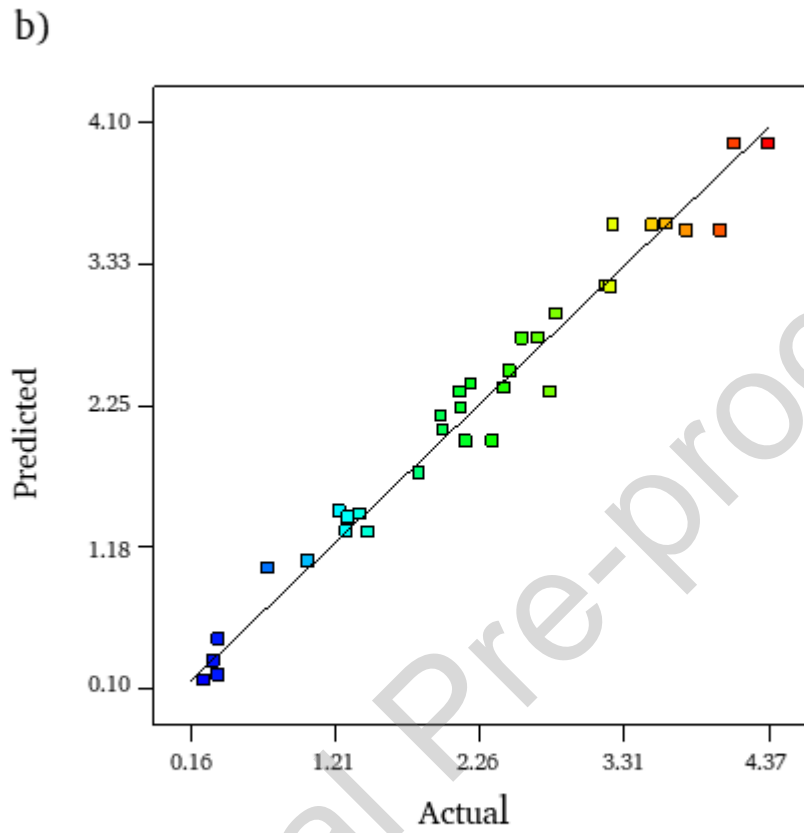
a)

Fig. 3. Empirical response surface fitted for Design 2 with cubic polynomic: a) 3D
visualization of fitted surface for H_2 and Ar; b) area predicted by the model vs actual
measured value.

Table 1

Instrumental details and operating conditions of the PVG-AAS system for Se (IV) determination

Instrument	Perkin Elmer AAnalyst 200
Cell temperature	940 ºC
EDL lamp current	280 mA
Measurement mode	Peak area
Slit width	2.3nm
Wavelength	196.03 nm

Photochemical vapor generation	
UV lamp	Power: 15 w
	Wavelength: 254 nm
PTFE reaction coil	Length: 3.4 m
	i.d. 1 mm
	o.d.1.5 mm
CH_3COOH concentration	5% (v/v)
HCOOH concentration	1.5% (v/v)

Carrier gas (Ar) flow rate	120 mL min^{-1}	
Auxiliary gas (H$_2$) flow rate	5 mL min^{-1}	
Sample flow rate	5 mL min^{-1}	

Table 2

Effect of potential interfering ions on Se instrument response. Results are expressed as mean concentration ± standard deviation (n = 3).

Interferent	Interferent concentration [mg L^{-1}]	Relative response [%]
As(III)	0.1	105±6
	1	104±6
Co (II)	1	102±5
	10	98±5
Cu (II)	1	57±3
	10	37±2
Fe (III)	1	101±6
	10	86±5
Mn (II)	1	91±5

	10	78±5
Ni (II)	1	95±6
	10	92±5
Sb(III)	0.1	107±5
	1	107±6
Zn (II)	1	100±5
	10	96±6

* The studied elements were tested at a concentration of Se of 100 μg L^{-1}

Table 3

Recovery test for five selected food samples*. Data are expressed as means concentration standard deviation ± standard deviation (n=3)

Garlic sample	Added Se (μg g^{-1})	Found (μg g^{-1})	Recovery (%)
S1	-	1.7 ±0.1	-
	0.3	1.9 ± 0.2	94 ± 6
	0.6	2.4 ± 0.2	107 ± 5
S2	-	1.6 ± 0.1	-
	0.3	1.8 ± 0.2	96 ± 5
	0.6	2.0 ± 0.2	91 ± 5
	-	1.8 ± 0.2	-

Sample			
S3	0.3	2.0 ± 0.2	96 ± 6
	0.6	2.5 ± 0.2	102 ± 6
	-	0.8 ± 0.1	-
S4	0.3	1.0 ± 0.1	95 ± 6
	0.6	1.4 ± 0.2	105 ± 5
	-	0.3 ± 0.0	-
S5	0.3	0.6 ± 0.0	93 ± 6
	0.6	1.0 ± 0.0	105 ± 5

*Se(IV) solution were added to the powdered garlic samples to perform the recovery test.

Table 4

Comparison of data determined by PVG-AAS and ICP-MS in different samples. Concentrations of Se are expressed in µg g^{-1} *

Sample	Se concentration (PVG-AAS)	Se concentration (ICP-MS)	Error (%)
G 1 (market)	5.1 ± 0.52	4.50 ± 0.45	13
G 2 (market)	0.36 ± 0.03	0.33 ± 0.03	9

G 3 (market)	< 0.11	< 0.08	-
G 4 (market)	< 0.11	< 0.08	-
GE 1 (enriched)	211 ± 19	205 ± 20	3
GE 2 (enriched)	112 ± 10	123 ± 12	-9
GE 3 (enriched)	248 ± 25	245 ± 25	1
GE 4 (enriched)	221 ± 22	230 ± 23	-4
N 1 (Argentina)	0.73 ± 0.07	0.71 ± 0.07	3
N 2 (Argentina)	0.56 ± 0.06	0.58 ± 0.05	-3
N 3 (Argentina)	< 0.11	< 0.08	-
N 4 (Argentina)	< 0.11	< 0.08	-
BN 1 (Brazil)	100 ± 10	103 ± 10	-3
BN 2 (Brazil)	78.8 ± 8.0	72.8 ± 7.2	8
BN 3 (Brazil)	30.4 ± 3.0	30.5 ± 2.9	0
BN 4 (Brazil)	40.7 ± 4.1	43.4 ± 4.3	-6

* Three set of replicates, each set consisting of three measurements.

CRediT authorship contribution statement

Jaime Palatnik: Conceptualization, Investigation, Methodology, Visualization, Validation, Writing – review & editing. Agustin Londonio: Conceptualization, Methodology, Writing – review & editing. Ezequiel Morzan: Software, Formal analysis. Rodolfo Wuilloud: Validation, Resources. Patricia Smichowski: Conceptualization, Writing – Original Draft, Writing – review & editing, Supervision.

Highlights

- The mixture of formic and acetic acids is an efficient photochemical reagent.

- The generation of volatile species of Se is achieved under mild conditions.

- UV-PVG-FI-AAS is a simple, sensitive and green profile technique.