



An accurate analytical method for the determination of cadmium: Ultraviolet based photochemical vapor generation-slotted quartz tube based atom trap-flame atomic absorption spectrophotometry

Çağdaş Büyükpınar^a, Süleyman Bodur^a, Elif Yazıcı^a, Zeynep Tekin^a, Nevim San^a,
Okan Tarık Komesli^b, Sezgin Bakırdere^{a,c,*}

^a Yıldız Technical University, Department of Chemistry, 34220 İstanbul, Turkey

^b Atatürk University, Department of Environmental Engineering, 25250 Erzurum, Turkey

^c Turkish Academy of Sciences (TÜBA), Piyade Street No: 27, Çankaya, 06690 Ankara, Turkey

ARTICLE INFO

Keywords:

Cadmium
Atomic absorption spectrometry
Photochemical vapor generation
T-shaped slotted quartz tube
Atom trapping

ABSTRACT

In this study, an eco-friendly and accurate analytical protocol was proposed for the determination of cadmium at trace levels. Prior to analysis in flame atomic absorption spectrophotometry (FAAS), an ultraviolet based photochemical vapor generation (PVG) method as a sample introduction system was employed to eliminate matrix effects. PVG system was combined with an online preconcentration technique called T-shaped slotted quartz tube-atom trapping (T-SQT-AT) for online preconcentration of cadmium in order to further increase analytical performance of the system. Hydrogen was used in the releasing of collected Cd atoms from the quartz surface. Under optimum conditions, limit of detection (LOD) and limit of quantitation (LOQ) of the developed method were specified as 2.5 ng/mL and 8.2 ng/mL, respectively. Percent recovery results for tap water and daphne tea samples were found to be between 87.6–105.3% and 90.9–103.3%, respectively.

1. Introduction

Cadmium as a transition metal in IIB group of the periodic table has carcinogenic and toxic properties for living organisms [1]. It is generally found as its metal ores and its mineral compounds such as cadmium oxide and cadmium sulfate in nature [2]. This element has been utilized in the production of batteries, plastics, metal containers, fertilizers, pigments and approximately thirty thousand tons cadmium are released to the ecosystem every year [2–4]. Therefore, human bodies can exposure to cadmium via water, air and food or industrial areas where cadmium is used. Cigarettes are also one of the major cadmium exposure way for human metabolism [4]. Cadmium concentration in tobacco was reported between 0.77 and 7.02 µg/g [5,6]. It is clearly known that cadmium has toxic effects on some organs like kidney and liver [7]. It can cause to the production of reactive oxygen, DNA damage and inhibition of DNA repair system [7–9]. Moreover, acceptable maximum level for cadmium in drinking water is recommended as 5.0 µg/L by United States Environmental Protection Agency (US EPA) [10].

In analytical atomic spectroscopy, chemical vapor generation (CVG) is frequently employed as a sample introduction system. Nonvolatile

metal species can be converted to their volatile forms (metal hydride, metal alkyl, metal halide and metal carbonyl etc.) by various pre-treatments of the sample [11]. CVG systems have several benefits such as the reduction of matrix effect, enhancement in detection power of analytical instruments and selectivity for analyte(s) [12]. In hydride generation systems, sodium borohydride is used as a reduction agent for the generation of volatile hydrides for favorable metals [13,14]. The reduction agent (NaBH₄) has been used for the formation of cadmium volatile species and it has been observed that cadmium hydrides decompose at room temperature. Cadmium atoms are generated at room temperature and absorb its specific radiation without flame [15,16]. On the other hand, hydride generation method requires expensive and unstable chemicals [11]. For this reason, a green alternative method called as ultraviolet based photochemical vapor generation (PVG) was developed to produce the volatile species of metal analyte(s) via utilizing low molecular weight organic acids (LMWOAs) as a photochemical reagent [12]. In literature, volatile cadmium species occurred in LMWOA media under UV irradiation are not well identified, on the other hand; CdH₂ and Cd(CH₃)₂ for its volatile species are suggested [17]. In 2003, Sturgeon et al. reported the first study about the PVG system as a sample

* Corresponding author.

E-mail address: bsegin@yildiz.edu.tr (S. Bakırdere).

<https://doi.org/10.1016/j.measurement.2021.109192>

Received 2 July 2020; Received in revised form 31 January 2021; Accepted 15 February 2021

Available online 20 February 2021

0263-2241/© 2021 Elsevier Ltd. All rights reserved.

introduction system for atomic absorption spectrometry [18]. This system has become a common analytical method to separate several metals from different matrices [19]. In literature, the PVG system was coupled to several analytical instruments such as atomic fluorescence spectrophotometry (AFS) [20], inductively coupled plasma-optical emission spectrometry (ICP-OES) [21], inductively coupled plasma – mass spectrometry (ICP-MS) [22] and graphite furnace atomic absorption spectrometry (GF-AAS) [23] for the determination of several analyte(s).

The detection limits of flame atomic absorption spectrophotometry (FAAS) are higher than some other spectrophotometric instruments (GFAAS, ICP-MS) due to low nebulization efficiency and short dwell time of atoms on the light path in FAAS systems [24]. There are several offline and online preconcentration methods to achieve lower detection limit for the analyte. Some offline methods such as dispersive liquid–liquid microextraction (DLLME) [25], switchable solvent-based liquid phase microextraction (SSLPME) [26], solid phase extraction (SPE) [27] and ultrasound-assisted magnetic dispersive microsolid-phase extraction (UA-M-D- μ SPE) [28] have been used to extract and preconcentrate the analyte from several matrices. Another way to solve these problems is to employ slotted quartz tube (SQT) with conventional FAAS systems. There are two main purposes of slotted quartz tube used in FAAS system: (a) enhancement in residence time of the atoms in the light path of FAAS, (b) trapping of the atoms in the inner surface of SQT [29]. In atom trap (AT) studies, SQT is acted as an online preconcentration tool with two main steps: (1) analyte atoms are adsorbed onto the inner surface of SQT under lean flame conditions and (2) the analyte atoms are released from the inner surface of SQT using organic solvents [30] or hydrogen gas [31].

In this study, PVG system equipped with T-SQT-AT system prior to FAAS analyses was established to determine cadmium at trace levels in tap water and daphne tea samples. Univariate optimization approach was carried out to specify optimum conditions for all variables. Under the optimum conditions, method validation and recovery experiments were performed for the determination of cadmium in tap water and daphne tea samples. This study is part of a project [32] and this is the first study on PVG-T-SQT-AT-FAAS combination for cadmium.

2. Experimental

2.1. Chemical and reagents

Cadmium, iron, selenium, lead, calcium and magnesium standard solutions (1000 mg/L) were purchased from High Purity Standards (North Charleston, USA). These solutions were used as stock solutions for the preparation of working standard solutions by diluting throughout the study. Formic acid (98–100% purity), acetic acid (>99.6% purity), propionic acid (99.0% purity), sodium chloride (99.0% purity), and potassium nitrate ($\geq 99.0\%$ purity) were purchased from Merck (Darmstadt, Germany). Elga 3 Water Purification System (High Wycombe, England) was utilized to obtain deionized water (resistivity of 18.2 M Ω .cm). High purity argon and hydrogen gases were attained from a gas supplier (Istanbul, Turkey).

2.2. Instrumentation

An atomic absorption spectrophotometer system (ATI UNICAM 929 AA, UNICAM – England) with a burner head was used in the quantitative determination of cadmium. Slit width, emission wavelength and operation current for cadmium hollow cathode lamp (HCL) were 0.5 nm, 228.8 nm and 2.0 mA, respectively. A deuterium hollow cathode lamp was utilized for background correction. Dimensions of the T-SQT were 16.0 cm length, 6.0 cm length of T part in T-SQT, 1.8 cm outer diameter, 1.5 cm inner diameter, 5.8 cm entrance slot and 2.0 cm exit slot. Additionally, two air knives were placed at both edges of the T-SQT system in order to prevent horn-shaped flame extensions from damaging FAAS components. A peristaltic pump (MiniPuls3, Gilson,

Massachusetts, USA) was used to transport the standard/sample solution throughout the sample line. A UV radiation photoreactor with a unique design was produced in laboratory and consisted of two parts: (1) one UV radiation source (Sylvania T5 type with G16W T5 HO product name, Feilo Sylvania, Turkey) and (2) one tubing line to treat sample solution with UV irradiation during its transfer into gas liquid separator (GLS). The source emits UV radiation in UV-C region (approximately 85%) with a peak at 253.7 nm. The tubing inside the reactor is made of quartz material, which has no absorption in UV region in order to maximize the light-analyte interaction. The quartz tubing was produced using eight equal quartz tube connected to each other in a zigzag pattern. The internal volume of the tubing was approximately 15.2 mL. The UV source was placed to the center of the tubing part in order to enhance the photon permeation yield for the formation of the radicals from LMWOA. The inner surface of the container of the reactor was covered with aluminum foil to protect laboratory personnel. GLS has a spray chamber design with a spherical shape. The interior volume of GLS was about 65 cm³. The nebulizer is concentric with the chamber to spray the liquid droplets to the inner walls. A cylindrical tube is extended towards the bottom of the chamber to prevent the liquid sample to be dragged by the argon gas to the atomizer. The dimensions of cylindrical tube were 40 mm of height, 10 mm of outer diameter and 6 mm of inner diameter. Fig. 1 shows PVG-T-SQT-AT-FAAS system [32].

2.3. Procedure

The standard/sample solutions were acidified with 8.0 M propionic acid for the initial step. Next, each acidified sample/standard solution was sent to the PVG system for 6.0 min using the peristaltic pump. The flow rate of the sample/standard solutions was fixed at 3.8 mL/min with help of the peristaltic pump. The acidified solution was exposed to UV radiation for 4.0 min via fixing the peristaltic pump at a certain flow rate. When the first drop of the acidified solution entered the GLS, the valve for the carrier gas (argon) was rapidly turned on in order to transfer volatile species of the analyte into the T-SQT system. The volatile analyte species were trapped onto the T-SQT surface at a lean flame for a period of 6.0 min. The carrier gas valve was turned off after the sample was dripped to GLS completely. Finally, the hydrogen gas was sent into the T-SQT system to release all trapped analyte atoms from the T-SQT inner surface and sharp analytical signals for target analyte were obtained. The optimum conditions for the PVG-T-SQT-AT-FAAS system are represented in Table 1.

2.4. Samples

Tap water sample was taken from the Davutpaşa Campus of Yıldız Technical University located in İstanbul, Turkey. The sample was filled into a pre-cleaned polypropylene bottle. Next, sample portions were separately taken into volumetric flasks and 30.1 mL of 13.3 M propionic acid was added into each flask. Then, tap water samples were individually spiked to 50, 100 and 200 ng/mL of Cd and then filled to 50 mL with deionized water.

A commercial brand of daphne tea sample was purchased from a local market in İstanbul, Turkey. Daphne tea leaves (2.50 g) was weighed into a volumetric flask and diluted to 250 mL with drinking water. Then, the mixture was boiled for 15 min and cooled to room temperature. The same spiking procedure was followed for daphne tea solution spiked in the range of 60–180 ng/mL.

In interference studies, selenium, iron, lead, calcium, magnesium, sodium, potassium, nitrate and chloride were selected as possible interferants for the developed method. Two cadmium standard solutions (0.67 μ M/75 μ g/L) were spiked with interferants to 1:1 and 1:10 analyte/interferent molar ratios. Selenium, iron, lead, calcium and magnesium solutions were prepared by diluting their individual standard solutions while sodium chloride and potassium nitrate salts were used for their individual ions.

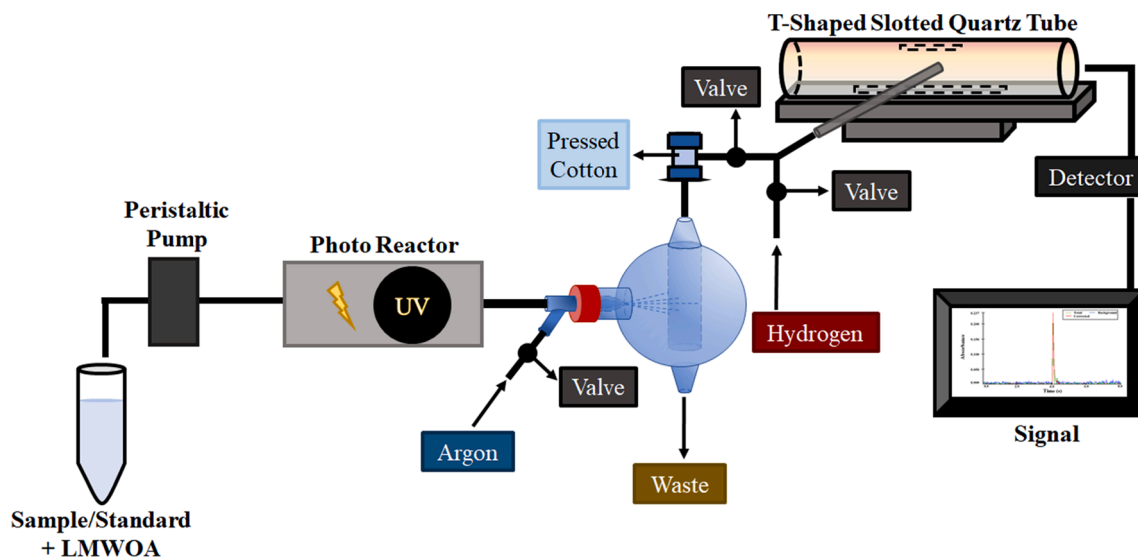


Fig. 1. PVG-T-SQT-AT-FAAS system schematic diagram.

Table 1
Optimum parameters of PVG-T-SQT-AT-FAAS system.

Parameter	Optimum value	Reference
LMWOA type	Propionic acid	[33]
LMWOA concentration	8.0 M	[33]
UV irradiation period	4.0 min	Present study
Flame type	Fuel-lean flame	Present study
Acetylene flow rate	8.0 L/h	Present study
Oxidant flow rate	28.0 L/h	Present study
T-SQT-AT height	0.0 mm	Present study
Hydrogen flow rate	430 mL/min	Present study
Argon flow rate	870 mL/min	Present study
Trapping period	6.0 min	Present study

3. Result and discussions

3.1. T-SQT-AT system optimizations

In this section, system parameters including flame type, T-SQT-AT height, hydrogen flow rate, carrier gas flow rate and trapping period were systematically optimized to lower the detection limit. All parameters were evaluated by univariate optimization and optimum values were determined with respect to the highest mean of triplicate measurements. The experimental conditions for PVG method were optimized in our previous work and optimum conditions were used throughout this study [33]. Although the optimum UV irradiation period for cadmium was determined as 9.0 min, it was too long for a single analysis and would negatively affect sample throughput, hence; 4.0 min was chosen as optimum value instead.

The composition of flame is of importance for the efficient adsorption of atoms onto the inner surface of T-SQT as the adsorption of atoms is inversely proportional to the temperature of flame [30]. Hence, the composition of flame was investigated as fuel-lean flame (8.0 L/h), stoichiometric flame (12.0 L/h) and fuel-rich flame (16 L/h) with respect to acetylene flow rate to attain the optimum flame composition. As expected, lean flame had the highest absorbance values; therefore, it was determined as optimum flame type. No absorbance signals were observed with the experiments conducted with stoichiometric and fuel-rich flames.

The analyte atoms after the atomization process were trapped onto the inner surface of T-SQT to concentrate the analyte atoms in the light path. The distance between the T-SQT and burner head can affect flame motion and amount in the T-SQT system. Therefore, the T-SQT height

values from the burner head were tested in the range of 0.0 and 2.0 mm. As a result of this optimization, the highest signals were obtained at 0.0 mm which had also lower standard deviation than other height values.

Hydrogen gas was used to release the trapped cadmium from the inner surface of quartz tube. Hence, optimization of the hydrogen flow rate for the revolatilization of adsorbed atoms provides a control over the signal shapes to obtain narrower and symmetric signals. During optimization, hydrogen flow rate was changed between 7.8 and 730.5 mL/min and the optimum value was chosen as 430 mL/min (Figure S1) that yielded the highest signal to noise ratios.

The analyte species separated from the liquid matrix in the GLS were transferred into the T-SQT via argon gas as it is also used to nebulize the liquid sample. With increased flow rates the separation and transfer of the volatile species are achieved more efficiently though risk of excess dilution of the analyte may occur after a point. Therefore, flow rate of the carrier gas was optimized using the values between 10 and 870 mL/min to obtain maximum trap efficiency. Argon flow rates higher than 870 mL/min were not tried for the risk of escaping liquid into the atomizer line. Maximum absorbances were recorded at 870 mL/min flow rate (Figure S2) and hence it was selected as optimum argon flow rate.

The height of signal and the number of trapped analyte atoms are directly proportional [34], thus; trapping period is the decisive variable for the atom trap performance. During optimization, standard solutions were sent to the PVG-T-SQT-AT-FAAS system with periods between 1.0 and 6.0 min with 1.0 min intervals to obtain the maximum signal to noise ratio. As a result, 6.0 min trapping period was selected as the optimum value (Fig. 2). In addition, longer trapping periods than 6.0 min were not tested in terms of sample throughput.

3.2. Analytical figures of merit

Cadmium standard solutions between 10.0 µg/L and 500 µg/L were sent to the PVG-T-SQT-AT-FAAS system in order to evaluate system performance under the optimum experimental conditions given in Table 1. The cleaning procedure with deionized water for the proposed system was applied for 30 s after each measurement. Blank sample was sent to the system to control the analyte signal caused by memory effect; no signal was observed. LOD, LOQ, dynamic range, EDR and coefficient of determination (R^2) for the PVG-T-SQT-AT-FAAS system are given in Table 2 in addition to the analytical performance of FAAS system. LOD and LOQ values for both systems were calculated via multiplying 3 and 10 times of s_{LC} (standard deviation of the lowest concentration in the

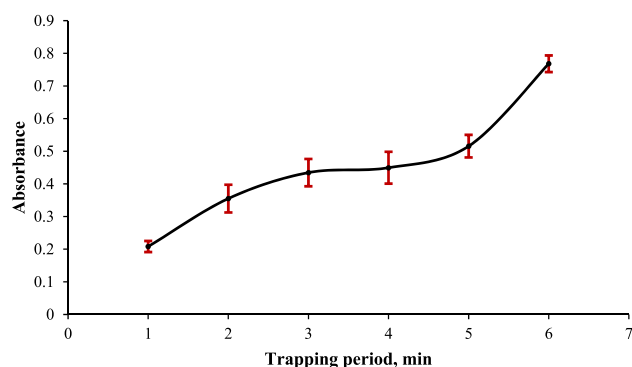


Fig. 2. Optimization of trapping period ($n = 3$). The concentration of standard solution acidified, organic acid type/concentration, UV irradiation period, flame type, hydrogen flow rate, argon flow rate, T-SQT height and sample flow rate were 250 $\mu\text{g/L}$, propionic acid/8.0 M, 4.0 min, lean flame, 430 mL/min, 870 mL/min, 0.0 mm and 3.8 mL/min, respectively.

linear calibration plot) and dividing these values to m_{CP} (slope of the calibration plot), respectively. As seen in the results, sensitivity of the FAAS system was improved by 106 folds using PVG-T-SQT-AT-FAAS system based on the comparison of slopes.

3.3. Interference studies

LMWOA based PVG system is not a selective method for only cadmium [17]. Other metals in the matrix could form their volatile species by the proposed procedure in this study. Negative/positive interference effects on the analyte could be observed because of the presence of interfering species. Therefore, effects of cations (selenium, iron, lead, calcium, magnesium, sodium and potassium) and anions (nitrate and chloride) were investigated at the same molar concentration with cadmium and 10 folds higher molar concentration. The preparation of solutions was clarified in Section 2.4. Cadmium signal was directly compared with the solutions consisting of 1:1 and 1:10 M ratios of analyte/interferants to calculate the effects of cations and anions on the analyte signal. The total effects of these interferants on the analyte were not significant for 1:10 ratio presented in the Fig. 3. In contrast, 23% decrease in absorbance was observed with the solution at 1:1 ratio of molar ratios of analyte/interferants. It is clear that presence of these ions has a depression effect on analyte signal. The results with the 1:10, on the other hand, can be linked to different depression and increasing effects of various ions.

3.4. Recovery tests

Under the optimum experimental conditions, the developed analytical method was applied to tap water and daphne tea samples to highlight the method accuracy and applicability. Both samples were

analyzed by the developed system for cadmium content resulting in no analytical signal. After blank analyses, the tap water and daphne tea samples were diluted 100 times and prepared by the procedure detailed in Section 2.4. Three different spiked concentrations (50, 100 and 200 ng/mL) found in the dynamic range of the developed method were tested for tap water sample. Percent recovery results for each spiked sample were calculated between 87.6 and 105.3% according to the results of triplicate measurements. Matrix matching calibration strategy was employed to calculate recovery results for daphne tea sample due to its negative matrix effect on the analyte signal. Three different spiked concentrations (80, 120 and 160 ng/mL) were sent to the system and recovery results were calculated in the range of 90.9 and 103.3%. The percent recovery results with their standard deviations for both matrices are presented in Table 3. With respect to all measurements, the method developed can be utilized for precise and accurate cadmium determination in tap water and daphne tea samples.

4. Conclusion

A cheap, precise and accurate analytical method called as PVG-T-SQT-AT-FAAS was developed to determine cadmium in tap water and daphne tea samples. This system was based on the combination of PVG and T-SQT-AT systems prior to measurement in FAAS system. Under the optimum experimental conditions, 106 folds enhancement in sensitivity was obtained when the calibration plot slopes of the conventional FAAS system and the developed method were compared to each other. LOD and LOQ values for the proposed method were recorded as 2.5 and 8.2 $\mu\text{g/L}$, respectively. The proposed method was applied to environmental (tap water) and food (daphne tea) samples to check its applicability and high recovery values validate the method's applicability to both

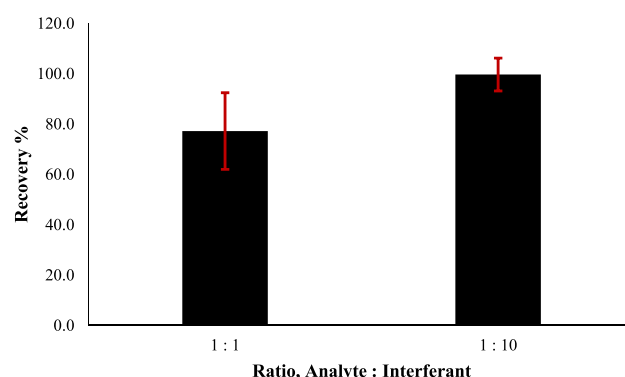


Fig. 3. Effect of interferants on recovery with respect to different ratios ($n = 3$). The organic acid type/concentration, UV irradiation period, flame type, hydrogen flow rate, argon flow rate, T-SQT height and sample flow rate were propionic acid/8.0 M, 4.0 min, lean flame, 430 mL/min, 870 mL/min, 0.0 mm, 3.8 mL/min and 6.0 min, respectively.

Table 2

Analytical performance comparison for the methods for cadmium determination.

System	LOD ^a	LOQ ^b	Dynamic Range	EDR ^c	Correlation of determination	Reference
FAAS	0.14 mg/L	0.47 mg/L	0.50–10.0 mg/L	$y = 0.0369x + 0.0104$	0.9999	Present study
PVG-T-SQT-AT-FAAS	2.5 $\mu\text{g/L}$	8.2 $\mu\text{g/L}$	0.01–0.20 mg/L	$y = 3.9372x + 0.0044$	0.9971	Present study
DBD-AES ^d	11.9 $\mu\text{g/kg}$	–	–	–	–	[35]
HG-AFS ^e	20 $\mu\text{g/kg}$	–	–	–	–	[36]
SUPRAS/TS-FF-AAS ^f	0.11 $\mu\text{g/L}$	0.36 $\mu\text{g/L}$	0.36–7.50 $\mu\text{g/L}$	–	–	[37]

^a LOD: Limit of detection.

^b LOQ: Limit of quantification.

^c EDR: Equation of dynamic range.

^d DBD-AES: Dielectric barrier discharge-atomic emission spectrometry.

^e HG-AFS: Hydride generation-atomic fluorescence spectrometry.

^f SUPRAS/TS-FF-AAS: Supramolecular solvent-based microextraction/thermospray flame furnace atomic absorption spectrometry.

Table 3

Recovery results with their standard deviation for tap water sample.

Sample	Spiked Concentration, ng/mL	Recovery %	± Standard deviation *
Tap water	50	87.6	2.5
	100	105.3	6.8
	200	103.6	6.4
Daphne tea	80	90.9	3.3
	120	103.3	2.1
	160	98.2	1.5

* Uncertainties (±): Standard deviation for n = 3.

matrices. The developed method promoted green chemistry by reducing chemical usage and harmful waste.

CRedit authorship contribution statement

Çağdaş Büyükpınar: Conceptualization, Methodology, Validation. **Süleyman Bodur:** Conceptualization, Methodology, Validation. **Elif Yazıcı:** Conceptualization, Methodology, Validation. **Zeynep Tekin:** Conceptualization, Methodology, Validation. **Nevim San:** Conceptualization. **Okan Tarık Komesli:** Conceptualization, Methodology. **Sezgin Bakırdere:** Supervision, Project administration, Writing - review & editing.

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.

Acknowledgement

This work was supported with project number of 117Z380 by The Scientific and Technological Research Council of Turkey (TÜBİTAK).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.measurement.2021.109192>.

References

- [1] M. Cataldi, C. Vigliotti, V. Sblendorio, C. Ferrara, Cadmium, in: Ref. Modul. Biomed. Sci., Elsevier, 2017. doi: 10.1016/B978-0-12-801238-3.99380-2.
- [2] A. Frischi, H. Choudhury, Cadmium, in: Int. Encycl. Public Heal., Elsevier, 2017; pp. 316–319. doi: 10.1016/B978-0-12-803678-5.00043-6.
- [3] I. Thornton, Sources and pathways of cadmium in the environment, IARC Sci. Publ. (1992) 149–162.
- [4] M. Méndez-Armenta, C. Ríos, Cadmium neurotoxicity, in: Environ. Toxicol. Pharmacol., Elsevier, 2007; pp. 350–358. doi: 10.1016/j.etap.2006.11.009.
- [5] D. Reyes-Hinojosa, C.A. Lozada-Pérez, Y. Zamudio Cuevas, A. López-Reyes, G. Martínez-Nava, J. Fernández-Torres, A. Olivós-Meza, C. Landa-Solis, M. Gutiérrez-Ruiz, E. Rojas del Castillo, K. Martínez-Flores, Toxicity of cadmium in musculoskeletal diseases, Environ. Toxicol. Pharmacol. (2019), 103219, <https://doi.org/10.1016/j.etap.2019.103219>.
- [6] D. Hutchinson, Cadmium, one of the villains behind the curtain: Has exposure to cadmium helped to pull the strings of seropositive rheumatoid arthritis pathogenesis all along? Int. J. Rheum. Dis. 18 (2015) 570–573, <https://doi.org/10.1111/1756-185X.12673>.
- [7] H. Zhang, M. Reynolds, Cadmium exposure in living organisms: a short review, Sci. Total Environ. 678 (2019) 761–767, <https://doi.org/10.1016/j.scitotenv.2019.04.395>.
- [8] F. Cao, T. Zhou, D. Simpson, Y. Zhou, J. Boyer, B. Chen, T. Jin, M. Cordeiro-Stone, W. Kaufmann, p53-dependent but ATM-independent inhibition of DNA synthesis and G2 arrest in cadmium-treated human fibroblasts, Toxicol. Appl. Pharmacol. 218 (2007) 174–185, <https://doi.org/10.1016/j.taap.2006.10.031>.
- [9] Z. Jianhua, X. Lian, Z. Shuanlai, D. Juan, Y. Shuanxi, DNA lesion and Hprt mutant frequency in rat lymphocytes and V79 Chinese Hamster lung cells exposed to cadmium, J. Occup. Health. 48 (2006) 93–99, <https://doi.org/10.1539/joh.48.93>.
- [10] WQA, WQA Technical Fact Sheet: Cadmium HEALTH EFFECTS TREATMENT METHODS Residential Point-of-Entry Point-of-Use, (2013) 1–4. <http://www.epa.gov/safewater/pdfs/factsheets/ioc/cadmium.pdf>.
- [11] Y. He, X. Hou, C. Zheng, R.E. Sturgeon, Critical evaluation of the application of photochemical vapor generation in analytical atomic spectrometry, Anal. Bioanal. Chem. 388 (2007) 769–774, <https://doi.org/10.1007/s00216-006-1044-7>.
- [12] R.E. Sturgeon, X. Guo, Z. Mester, Chemical vapor generation: are further advances yet possible? Anal. Bioanal. Chem. 382 (2005) 881–883, <https://doi.org/10.1007/s00216-005-3118-3>.
- [13] A.D. Ulivo, Atomic Absorption Spectrometry | Vapor Generation ☆, Encycl. Anal. Sci. (2018) 149–159. doi: 10.1016/B978-0-12-409547-2.00025-1.
- [14] A. Ramesh Kumar, P. Riyazuddin, Mechanism of volatile hydride formation and their atomization in hydride generation atomic absorption spectrometry, Anal. Sci. 21 (2005) 1401–1410, <https://doi.org/10.2116/analsci.21.1401>.
- [15] A. Sanz-Medel, M.C.V.H.Y. Temprano, N.B. García, M.R.F. De La Campa, The use of surfactants to obtain cadmium atoms at room temperature and its application for the cold vapour AAS determination of the metal, Anal. Proc. Incl. Anal. Commun. 32 (1995) 49–52, <https://doi.org/10.1039/A19953200049>.
- [16] A. Sanz-Medel, M.C. Valcés-Hevia y Temprano, N. Borden García, M.R. Fernandez de la Campa, Generation of Cadmium Atoms at Room Temperature Using Vesicles and Its Application to Cadmium Determination by Cold Vapor Atomic Spectrometry, Anal. Chem. 67 (1995) 2216–2223. doi: 10.1021/ac00109a048.
- [17] D. Leonori, R.E. Sturgeon, A unified approach to mechanistic aspects of photochemical vapor generation, J. Anal. At. Spectrom. 34 (2019) 636–654, <https://doi.org/10.1039/c8ja00354h>.
- [18] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, UV vapor generation for determination of selenium by heated quartz tube atomic absorption spectrometry, Anal. Chem. 75 (2003) 2092–2099, <https://doi.org/10.1021/ac020695h>.
- [19] Z. Zou, J. Hu, F. Xu, X. Hou, X. Jiang, Nanomaterials for photochemical vapor generation-analytical atomic spectrometry, TrAC Trends Anal. Chem. 114 (2019) 242–250, <https://doi.org/10.1016/j.trac.2019.03.012>.
- [20] C. Zheng, Q. Ma, L. Wu, X. Hou, R.E. Sturgeon, UV photochemical vapor generation-atomic fluorescence spectrometric determination of conventional hydride generation elements, Microchem. J. 95 (2010) 32–37, <https://doi.org/10.1016/j.microc.2009.09.010>.
- [21] C. Zheng, R.E. Sturgeon, C. Brophy, X. Hou, Versatile thin-film reactor for photochemical vapor generation, Anal. Chem. 82 (2010) 3086–3093, <https://doi.org/10.1021/ac100229k>.
- [22] P. Grinberg, R.E. Sturgeon, Photochemical vapor generation of iodine for detection by ICP-MS, J. Anal. At. Spectrom. 24 (2009) 508–514, <https://doi.org/10.1039/b814272f>.
- [23] C. Zheng, R.E. Sturgeon, X. Hou, UV photochemical vapor generation and in situ preconcentration for determination of ultra-trace nickel by flow injection graphite furnace atomic absorption spectrometry, J. Anal. At. Spectrom. 24 (2009) 1452–1458, <https://doi.org/10.1039/b909962j>.
- [24] A.A. Brown, A. Taylor, Applications of a slotted quartz tube and flame atomic-absorption spectrometry to the analysis of biological samples, Analyst. 110 (1985) 579–582, <https://doi.org/10.1039/AN9851000579>.
- [25] A. Sixto, A. Mollo, M. Knochen, Fast and simple method using DLLME and FAAS for the determination of trace cadmium in honey, J. Food Compos. Anal. 82 (2019), 103229, <https://doi.org/10.1016/j.jfca.2019.06.001>.
- [26] E. Vessally, E. Ghorbani-Kalhor, R. Hosseinzadeh-Khanmiri, M. Babazadeh, A. Hosseini, F. Omid, M.H. Ebrahimi, Application of switchable solvent-based liquid phase microextraction for preconcentration and trace detection of cadmium ions in baby food samples, J. Iran. Chem. Soc. 15 (2018) 491–498, <https://doi.org/10.1007/s13738-017-1249-z>.
- [27] K. Prasad, P. Gopikrishna, R. Kala, T.P. Rao, G.R.K. Naidu, Solid phase extraction vis-à-vis coprecipitation preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and determination by FAAS, Talanta 69 (2006) 938–945, <https://doi.org/10.1016/j.talanta.2005.11.040>.
- [28] B. Fahimrad, A. Asghari, M. Rajabi, Magnetic graphitic carbon nitride nanoparticles covalently modified with an ethylenediamine for dispersive solid-phase extraction of lead(II) and cadmium(II) prior to their quantitation by FAAS, Microchim. Acta. 184 (2017) 3027–3035, <https://doi.org/10.1007/s00604-017-2273-5>.
- [29] S. Bakırdere, F. Aydın, E.G. Bakırdere, S. Titretir, I. Akdeniz, I. Aydın, E. Yıldırım, Y. Arslan, From mg/kg to pg/kg levels: a story of trace element determination: a review, Appl. Spectrosc. Rev. 46 (2011) 38–66, <https://doi.org/10.1080/05704928.2010.520179>.
- [30] O.Y. Ataman, Vapor generation and atom traps: Atomic absorption spectrometry at the ng/L level, Spectrochim. Acta - Part B At. Spectrosc. 63 (2008) 825–834, <https://doi.org/10.1016/j.sab.2008.03.013>.
- [31] H. Uslu, Ç. Büyükpınar, T. Unutkan, H. Serbest, N. San, F. Turak, S. Bakırdere, A novel analytical method for sensitive determination of lead: hydrogen assisted T-shape slotted quartz tube-atom trap-flame atomic absorption spectrometry, Microchem. J. 137 (2018) 155–159, <https://doi.org/10.1016/j.microc.2017.10.015>.
- [32] S. Bakırdere, Determination of Pb, Cd, Ni, Co at trace levels by ultraviolet photochemical volatile compounds generation-atom trap-flame atomic absorption spectrometry system, The Scientific and Technological Research Council of Turkey (TÜBİTAK) with a grant number of 117Z380, 2020.
- [33] Ç. Büyükpınar, S. Bodur, N. San, O.T. Komesli, S. Bakırdere, Photochemical vapor generation based accurate determination of cadmium in wastewater using novel photoreactor and gas-liquid separators using flame atomic absorption spectrometry with matrix matching calibration, Anal. Lett. (2020), <https://doi.org/10.1080/00032719.2020.1858308>.
- [34] S. Titretir, A.I. Şik, Y. Arslan, O.Y. Ataman, Sensitivity improvement for antimony determination by using in-situ atom trapping in a slotted quartz tube and flame

- atomic absorption spectrometry, *Spectrochim Acta - Part B At. Spectrosc.* 77 (2012) 63–68, <https://doi.org/10.1016/j.sab.2012.09.001>.
- [35] J. Jiang, Z. Li, Y. Wang, X. Zhang, K. Yu, H. Zhang, J. Zhang, J. Gao, X. Liu, H. Zhang, W. Wu, N. Li, Rapid determination of cadmium in rice by portable dielectric barrier discharge-atomic emission spectrometer, *Food Chem.* 310 (2020), 125824, <https://doi.org/10.1016/j.foodchem.2019.125824>.
- [36] H. Yu, X. Ai, K. Xu, C. Zheng, X. Hou, UV-assisted Fenton digestion of rice for the determination of trace cadmium by hydride generation atomic fluorescence spectrometry, *Analyst.* 141 (2016) 1512–1518, <https://doi.org/10.1039/c5an02068a>.
- [37] F.A.C. Suquila, G.L. Scheel, F.M. de Oliveira, C.R.T. Tarley, Assessment of ultrasound-assisted extraction combined with supramolecular solvent-based microextraction for highly sensitive cadmium determination in medicinal plant sample by TS-FF-AAS, *Microchem. J.* 145 (2019) 1071–1077, <https://doi.org/10.1016/j.microc.2018.12.011>.