Title

Speciation analysis of inorganic Sb leached from InSb thin films by hydride generation–microwave plasma-atomic emission spectroscopy

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Abstract

Sb speciation analysis is important in relation to industrial exposure or environmental release because of the large difference in toxicity between Sb^{III} and Sb^{V}. In this study, the release of Sb species from a semiconductor material (undoped and Bi-doped InSb thin films) in 0.1 mol/L sodium acetate buffer was investigated using hydride generation–microwave plasma-atomic emission spectroscopy (HG–MP-AES). Total Sb was determined using our previously reported method, and Sb^{III} concentration was measured without reduction by potassium iodide and with a lower sodium tetrahydroborate/sodium hydroxide concentration. To estimate the Sb^{V} concentration, the Sb^{III} concentration was subtracted from the total Sb concentration. The Sb species were not changed by Bi doping, even though Bi doping suppressed the Sb elution from the thin films. A large fraction of Sb eluted as Sb^{III} during leaching for 28 days. This is the first Sb speciation analysis using HG–MP-AES of eluates from Sb-based materials. Sb speciation analysis using HG–MP-AES is cost effective, reliable, and requires only simple sample preparation.

Keywords Sb^{III} · Sb^{V} · MP-AES · Hydride generation · InSb · Leaching

Introduction

Sb is a metalloid element that is sometimes found as a free metal but is usually obtained as an oxide or sulfide (e.g., Sb_2O_3 and Sb_2S_3) from ores [1]. Sb is used in manufacturing flame retardants for plastics, fabrics, catalysts, and abrading agents [2]. Furthermore, Sb-based compound semiconductors are attractive materials with a high electron mobility, a high saturation velocity, and favorable optoelectronic properties in the infrared (IR) region [3–5]. Sb is also a toxic element [6], and its toxicity differs greatly among its chemical species and oxidation state. The toxicity of organic species is lower than that of inorganic species, and the toxicity of Sb^{III} is 10 times greater than that of Sb^{V} [7–9]. Hence, Sb speciation analysis is important.

Inorganic Sb speciation has been analyzed by combining chromatographic separation with high-performance liquid chromatography coupled with inductively coupled plasma-mass spectrometry [10, 11]. However, non-chromatographic methods are cheaper and easier than chromatographic methods. Non-chromatographic speciation analysis methods using electrothermal atomic absorption spectrometry [12], hydride generation (HG) atomic fluorescence spectrometry [13, 14], and HG-atomic absorption spectrometry [15–18] have been reported. Microwave plasma-atomic emission spectrometry (MP-AES) allows fast multi-element analysis in a sequential mode with good detection power and low maintenance costs [19]. We have previously reported a procedure for total Sb analysis using an HG–MP-AES with a multimode sample introduction system (MSIS) [20].

InSb thin films are applied to various optical devices, such as IR light-emitting diodes and IR sensors [21, 22]. In addition, the higher electron mobility of InSb (78,000 cm^2/Vs at 300 K) makes it suitable for use as a magnetic resistance element to detect the biomagnetic field in the body [23, 24]. Before InSb-based materials can be used in embedded

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devices, speciation of Sb eluted in physiological conditions must be examined. Therefore, in this work, speciation of Sb eluted from an InSb thin film under physiological conditions was performed by HG–MP-AES.

Experimental

Reagents

All reagents used in this study were at least analytical grade. Milli-Q water (> 18 mΩcm, Merck Millipore) was used to dilute the reagents. Sb^{III} standard stock solution (1000 mg/L, 3 mol/L HCl) was prepared by dissolving Sb^{III} chloride (0.192 g) in concentrated HCl (25 mL) and filled up the solution to 100 mL with water. Sb^V standard stock solution (1000 ppm) was prepared by dissolving potassium hexahydroxoantimonate (V) (0.108 g) in water (50 mL) by heating at 95 °C for 30 min.

Total Sb analysis

The total Sb concentration was measured by HG–MP-AES using an MP-AES system (Agilent 4200, Agilent Technologies) equipped with an MSIS (Agilent Technologies) as previously reported [20]. Before the analysis, Sb species in the samples and calibration standards were reduced with 20% KI and acidified with 1 N HCl. The reduced samples and a

NaBH$_4$/NaOH solution (3% (w/V) solution in 0.2% (w/V) NaOH) were introduced to the MSIS to generate hydride (Fig. 1). The unused flow pass to the MSIS was blocked. The calibration for total Sb is shown in Fig. 2a.

Speciation analysis of Sb

Sb^{III} level was determined based on selective HG according to previous methods with slight modifications [15–18]. The same method as the total Sb analysis was used except that no KI reduction was performed and the NaBH$_4$ concentration was lower. Sb^{III} in the samples and calibration standards (2.4 mL) were acidified with 1 N HCl (0.6 mL) without KI reduction. The samples and the NaBH$_4$/NaOH (0.4% (w/V) solution in 0.2% (w/V) NaOH) were introduced into the MSIS. The calibration for Sb^{III} is shown in Fig. 2b. Sb^V concentrations were calculated by subtracting the Sb^{III} concentrations from the total Sb concentrations (Fig. 1).

Method validation

To validate the analytical method for the Sb^{III} standard, Sb^{III} standard solution was subjected to MP-AES analysis to acquire the calibration curves. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as $LOD = 3\sigma/S$ and $LOQ = 10\sigma/S$ (in µg/L), respectively. σ is the standard deviation of 10 measurements of the blank

Fig. 1 Schematic of the analysis method for inorganic Sb speciation by hydride generation–microwave plasma-atomic emission spectroscopy with a multimode sample introduction system. **a** Total Sb and **b** Sb^{III} analyses
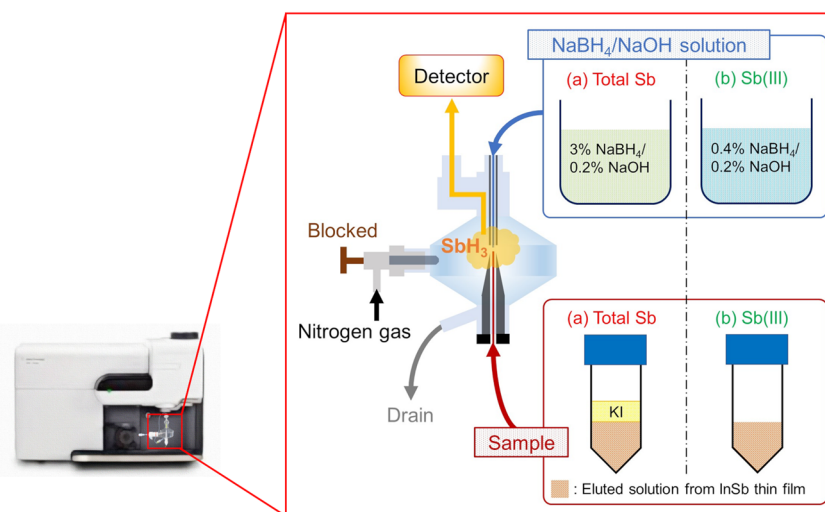
Step 1. Measurement of total Sb and Sb(III) concentrations.
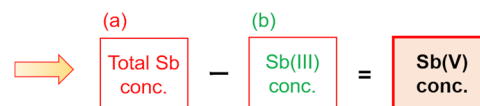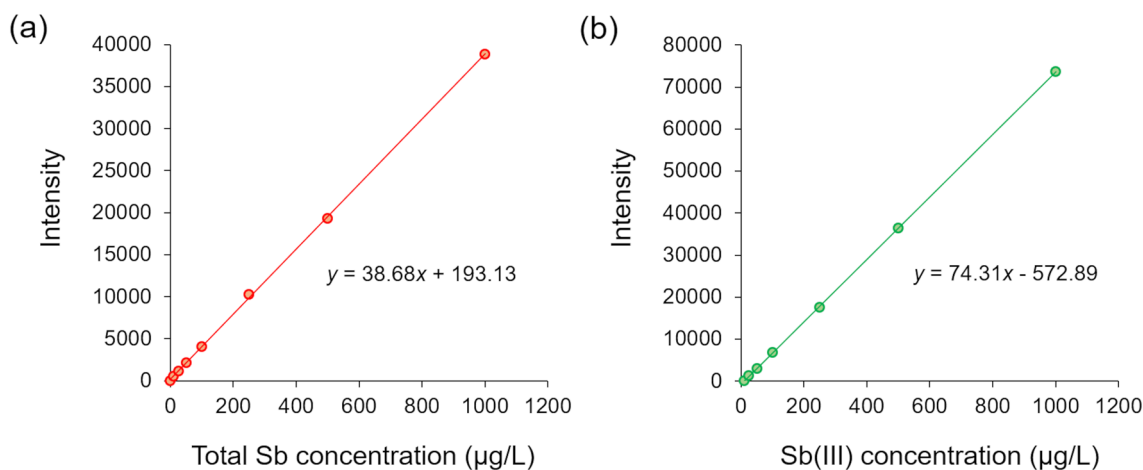
Step 2. Estimation of Sb(V) concentration.

Fig. 2 Calibration curve for **a** total Sb and **b** Sb^{III} determinations

solution and S is the calibration curve slope. By analyzing the Sb^{III} solution (20 µg/L) three times, the intra-day and inter-day repeatability were assayed. A recovery study was performed in solutions spiked with Sb^{III} and Sb^{V}. Sb^{III} and Sb^{V} standard solutions (10 µL each, 100 mg/L) were added to 0.1 mol/L sodium acetate buffer (50 mL) and recoveries for Sb^{III} and Sb^{V} were calculated.

Sb species eluted from undoped and Bi-doped InSb thin films

Undoped and Bi-doped InSb thin films of 640 nm thick were grown at 320 °C on quartz substrates (0.5 mm thick, 10 × 10 mm) and polyimide films (125 µm thick, 10 × 10 mm) by RF magnetron sputtering as previously reported [25]. In$_{0.5}$Sb$_{0.5}$ and In$_{0.5}$Sb$_{0.47}$Bi$_{0.03}$ sputtering targets were used for the undoped and Bi-doped InSb thin films, respectively. Bi content in the Bi-doped InSb thin film was 0.015 atom %, and Bi assisted the crystal growth of the InSb thin film [25]. The undoped and Bi-doped thin films (each $n = 1$) were soaked in 0.1 mol/L sodium acetate buffer (1.5 mL, pH 5) at room temperature for 28 days. After 1, 7, 14, and 28 days, the immersion solutions (500 µL) were collected, and the same volume of 0.1 mol/L sodium acetate buffer was supplied to the immersion solutions. The collected solutions were diluted with 1 N HNO$_3$ (4.5 mL). Speciation of Sb in the eluted solution was performed as described above. To confirm the matrix effect of Bi, the Bi-doped InSb thin film was immersed in 0.1 mol/L sodium acetate buffer (5 mL) for 7 days and total Sb and Sb^{III} in the solution (×1 and ×20 with sodium acetate buffer) was analyzed.

Results and discussion

Sb^{III} analysis by HG–MP-AES and method evaluation

To analyze Sb^{III}, the pretreatment used a lower NaBH$_4$ concentration and no KI addition to prevent Sb^{V} from being reduced to Sb^{III} (Fig. 1). Sb^{III} calibration standards (0–1000 µg/L) were analyzed and a linear calibration curve can be obtained (Fig. 2b, r = 0.99995). LOD and LOQ were found to be 0.02 µg/L and 0.07 µg/L, respectively. Intra-day and inter-day assays were conducted using the Sb^{III} solution (20 µg/L, $n = 3$) to evaluate the precision of the present method. The relative standard deviations (RSDs) for the Sb^{III} solution of the inter-day and intra-day assays were 3.16% and 2.39%, respectively. As shown in Table 1, The LOD, precision (RSD), and recovery of the present method were comparable to those of the previous methods by selective HG using atomic absorption spectroscopy.

The accuracy of the method for measuring Sb^{III} and Sb^{V} was assessed by the recovery from spiked sodium acetate buffer samples (Table 2). The Sb^{V} concentration was determined by subtracting the Sb^{III} concentration from the total Sb concentration. The recoveries of Sb^{III} and Sb^{V} from the spiked buffer samples were 102% and 88.8%, respectively, indicating good accuracy. In general, various kinds of interferences are inevitable in commonly used analytical atomic spectrometry techniques. However, MP-AES has the advantage of having relatively fewer interferences. It uses nitrogen plasma at a lower temperature (5000 K) than argon plasma (8000–10000 K) [26]; spectral interference is not significant and atomic emission spectral lines

Detection method	LOD[a] (µg/L)	RSD[b] (%)	Recovery (%)	References
FIA-HG-AAS[c]	0.007	0.4	–	[15]
HG-(batch)-AAS[d]	2.97	6.6	–	[15]
HG-AAS[e]	0.21	2.8	–	[15]
FIA-HG-AAS[c]	0.05	2.1	–	[16]
FS-HG-AAS[f]	–	5.80	–	[17]
FS-HG-AAS[f]	–	0.3–2.2	93–101	[18]
MSIS-HG–MP-AES[g]	0.02	3.16	90.9–95.4	This study

[a]Limit of detection for Sb[III]

[b]Relative standard deviation

[c]Flow injection analysis-hydride generation-atomic absorption spectroscopy

[d]Hydride generation-atomic absorption spectroscopy (batch mode)

[e]Hydride generation-atomic absorption spectroscopy (continuous flow)

[f]Fast sequential-hydride generation-atomic absorption spectroscopy

[g]Multimode sample introduction system-hydride generation–microwave plasma-atomic emission spectroscopy

Added (µg/L)		Found (µg/L)			Recovery (%)		
Sb[III]	Sb[V]	Sb[III]	Sb[Va]	Total Sb	Sb[III]	Sb[V]	Total Sb
20	20	20.4 ± 0.06	17.8 ± 0.64	38.1 ± 0.64	102	88.8	95.4

[a]Sb[V] concentrations were calculated by subtracting the Sb[III] concentrations from the total Sb concentrations

are simpler because most of the elements remain in the atomic state and this temperature is high enough to reduce chemical interference [27]. Moreover, nitrogen plasma is more inert compared with acetylene flame [27]. Therefore, this method enables Sb speciation without spectral and chemical interference.

Sb speciation eluted from undoped and Bi-doped InSb thin films

Sb speciation in aqueous solution is important because the Sb[III] toxicity is greater than that of Sb[V], and their treatment methods are different [28]. Accordingly, it is necessary to analyze the Sb species eluted from InSb thin films. In general, the etch rate when using acid solution is faster than that when using alkaline solutions because it depends on the crystal plane orientation in alkaline etching (anisotropic etching) but this dependence is not observed in acid etching (isotropic etching) [29]. Therefore, InSb may readily be eluted in acidic solutions. We have previously shown that In and Sb eluted from InSb-based thin films to a greater extent in 0.1 mol/L sodium acetate buffer (pH 5) than in other physiological conditions (distilled water and pH 9 Tris buffer) [5, 24]. Owing to these results, this pH 5 buffer was used in the present study.

The cumulative amount of eluted Sb[III] and Sb[V] in sodium acetate buffer (pH 5) from undoped InSb and Bi-doped InSb thin films over 28 days is shown in Fig. 3. Sb elution from the thin films showed no difference between the quartz and polyimide film substrates. Both undoped InSb on quartz substrate and undoped InSb on polyimide film are completely dissolved after immersion for 14 days (Fig. 3a, b). In contrast, Bi doping suppressed the Sb elution in pH 5 buffer; the cumulative amount of eluted Sb[III] and Sb[V] from Bi-doped InSb was lower than that from undoped InSb (Fig. 3), and InSb remained on substrates after immersion for 14 days (Fig. 3c, d). This is due to the increased crystallinity of InSb by Bi-doping [25]. The Sb species were the same for the undoped InSb and Bi-doped InSb thin films. After 1 day, more than 90% of the Sb eluted as Sb[III] from all the thin films, and a large fraction of Sb eluted as Sb[III] (about 80%) after 7, 14 and 28 days. These results are similar to that of a previous study of GaAs leaching. Ramos-Ruiz et al. reported the leaching behavior of particulate GaAs in aqueous solutions of pH 6.8, 7.9, and 8.5: As[III] accounted for 70–90% of the dissolved total As [30]. Sb speciation is function of pH and redox potential [31]. In a pH range of 2.7–10.4, Sb[III] exists as H_3SbO_3 or $Sb(OH)_3$, Sb[V] exists as $HsSbO_4^-$ or $Sb(OH)_6^-$ [1]: the eluted Sb species in this study may exist in these forms.
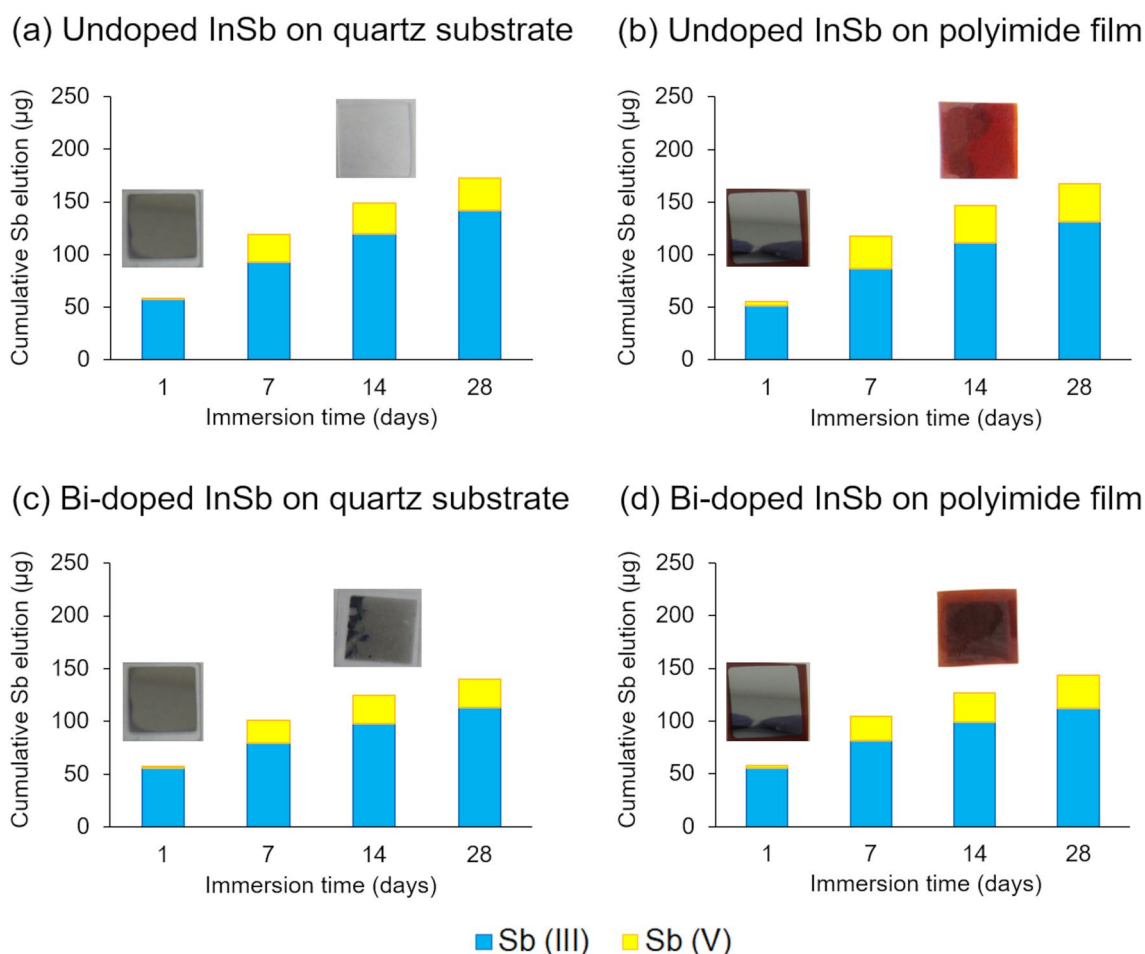
Fig. 3 Cumulative amount of Sb species leached from InSb thin films in 0.1 M sodium acetate buffer (pH 5). **a** Undoped InSb grown on a quartz substrate, **b** undoped InSb grown on a polyimide film, **c** Bi-doped InSb grown on a quartz substrate, and **d** Bi-doped InSb grown on a polyimide film. Insets show photographs of InSb and Bi-doped InSb thin films after 1 and 14 days

Conclusion

The release of Sb species from a semiconductor material (undoped and Bi-doped InSb thin films) in 0.1 mol/L sodium acetate buffer was investigated by HG–MP-AES. Although Bi doping suppressed the Sb elution from the thin films, it did not alter the Sb species. A large fraction of Sb eluted as Sb^{III} after leaching for 28 days. Sb speciation analysis using HG–MP-AES is cost effective and reliable, requires simple sample preparation, and can be used in engineering analysis.

Declarations

Conflict of interest The authors declare no conflicts of interest.

References

1. I. Herath, M. Vithanage, J. Bundschuh, Environ. Pollut. **223**, 545 (2017). https://doi.org/10.1016/j.envpol.2017.01.057
2. S. Sundar, J. Chakravarty, Int. J. Environ. Res. Public Health **7**, 4267 (2010). https://doi.org/10.3390/ijerph7124267
3. P.S. Dutta, H.L. Bhat, J. Appl. Phys. **81**, 5821 (1997). https://doi.org/10.1063/1.365356
4. N. Nishimoto, J. Fujihara, Phys. Status Solidi A **216**, 1800860 (2019). https://doi.org/10.1002/pssa.201800860
5. N. Nishimoto, J. Fujihara, Mater. Chem. Phys. **274**, 125160 (2021). https://doi.org/10.1016/j.matchemphys.2021.125160
6. J. Fujihara, N. Nishimoto, Int. J. Mod. Phys. B **35**, 2150297 (2021). https://doi.org/10.1142/S0217979221502970
7. R. Poon, I. Chu, P. Lecavalier, V.E. Valli, W. Foster, S. Gupta, B. Thomas, Food Chem. Toxicol. **36**, 20 (1998). https://doi.org/10.1016/S0278-6915(97)80120-2
8. A. Gonzalvez, M.L. Cervera, S. Armenta, M. de la Guardia, Anal. Chim. Acta **636**, 129 (2009). https://doi.org/10.1016/j.aca.2009.01.065

9. R. Miravet, J.F. López-Sánchez, R. Rubio, Anal. Chim. Acta **576**, 200 (2006). https://doi.org/10.1007/s00216-006-1077-y

10. Y. Morita, T. Kobayashi, T. Kuroiwa, T. Narukawa, Talanta **73**, 81 (2007). https://doi.org/10.1016/j.talanta.2007.03.005

11. M. Jabłońska-Czapla, K. Grygoyć, Environ. Sci. Pollut. Res. Int. **27**, 12358 (2020). https://doi.org/10.1007/s11356-020-07758-9

12. S. Wen, X. Zhu, Talanta **115**, 814 (2013). https://doi.org/10.1016/j.talanta.2013.06.057

13. H. Wu, X.C. Wang, B. Liu, Y.L. Liu, S.S. Li, J.S. Lu, J.Y. Tian, W.F. Zhao, Z.H. Yang, Spectrochim. Acta B **66**, 74 (2011). https://doi.org/10.1016/j.sab.2010.12.002

14. I.D. Gregori, W. Quiroz, H. Pinochet, J. Chromatogr. A **1091**, 94 (2005). https://doi.org/10.1016/j.chroma.2005.07.060

15. M.B. de la Calle Guntiñas, Y. Madrid, C. Cámara, Microchim. Acta **109**, 149 (1992). https://doi.org/10.1007/BF01243229

16. F.Y. Zheng, S.H. Qian, S.X. Li, X.Q. Huang, L.X. Lin, Anal. Sci. **22**, 1319 (2006). https://doi.org/10.2116/analsci.22.1319

17. F.O. Correia, T.S. Almeida, R.L. Garcia, A.F.S. Queiroz, P. Smichowski, G.O. da Rocha, R.G.O. Araujo, Environ. Geochem. Health **26**, 21416 (2019). https://doi.org/10.1007/s11356-019-04638-9

18. V.S. Ribeiro, S.O. Souza, S.S.L. Costa, T.S. Almeida, S.A.R. Soares, M.G.A. Korn, R.G.O. Araujo, Environ. Geochem. Health **42**, 2179 (2020). https://doi.org/10.1007/s10653-019-00488-z

19. V. Balaram, Microchem. J. **159**, 105483 (2020). https://doi.org/10.1016/j.microc.2020.105483

20. J. Fujihara, N. Nishimoto, Microchem. J. **157**, 104992 (2020). https://doi.org/10.1016/j.microc.2020.104992

21. A.A. Semakova, V.V. Romanov, K.D. Moiseev, N.L. Bazhenov, K.D. Mynbaev, J. Phys. Conf. Ser. **1482**, 012023 (2020). https://doi.org/10.1088/1742-6596/1482/1/012023

22. S.H. Zainud-Deen, H.A.E.A. Malhat, E.A.A. El-Refaay, Wirel. Pers. Commun. **115**, 893 (2020). https://doi.org/10.1007/s11277-020-07603-9

23. N. Nishimoto, J. Fujihara, Appl. Surf. Sci. **409**, 375 (2017). https://doi.org/10.1016/j.apsusc.2017.03.099

24. N. Nishimoto, J. Fujihara, Int. J. Mod. Phys. B **33**, 1950109 (2019). https://doi.org/10.1142/S0217979219501091

25. N. Nishimoto, J. Fujihara, Appl. Phys. A **128**, 550 (2022). https://doi.org/10.1007/s00339-022-05694-8

26. G.L. Donati, R.S. Amais, D. Schiavo, J.A. Nobrega, J. Anal. At. Spectrom. **28**, 755 (2013). https://doi.org/10.1039/C3JA30344F

27. V. Balaram, V. Dharmendra, P. Roy, C. Taylor, C.T. Kamala, M. Satyanarayanan, P. Kar, K.S.V. Subramanyam, A.K. Raju, A. Krishnaiah, At. Spectrosc. **35**, 65 (2014). https://doi.org/10.46770/AS.2014.02.003

28. P.A. Nishad, A. Bhaskarapillai, Chemosphere **277**, 130252 (2021). https://doi.org/10.1016/j.chemosphere.2021.130252

29. A.B.A. Prakash, J.G. Jency, M.C. Mathew, in *IJCA Proceedings on International Conference on Innovations in Intelligent Instrumentation, Optimization and Electrical Sciences ICIIIOES* vol 7 (2013), p. 26

30. A. Ramos-Ruiz, J.A. Field, W. Sun, R. Sierra-Alvarez, Waste Manag. **77**, 1 (2018). https://doi.org/10.1016/j.wasman.2018.04.027

31. S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, Environ. Pollut. **158**, 1169 (2010). https://doi.org/10.1016/j.envpol.2009.10.045