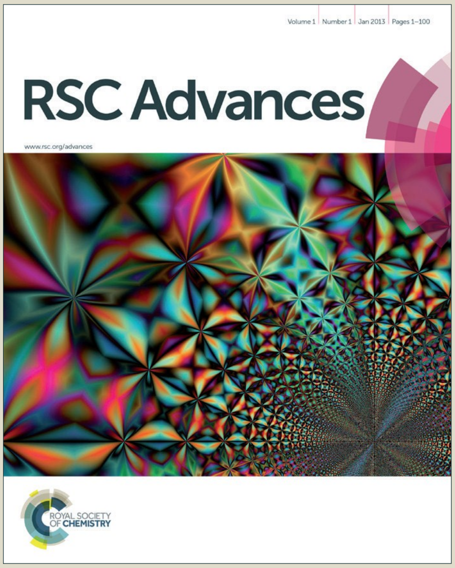
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Switchable solvent based liquid phase microextraction of mercury from environmental samples: A green aspect

Mansoor Khan [1, 2], Mustafa Soylak[1*]

[1] Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri-TURKEY

[2] Institute of Chemical Sciences, University of Peshawar, Peshawar-Pakistan

Abstract

A novel and environmental friendly approach by using switchable solvent based liquid phase microextraction (SPS-LPME), followed by Uv-Vis-spectrophotometric determination has been developed for preconcentration and determination of mercury. Dithizone was used as complexing reagent that forms hydrophobic complex with Hg(II) which was determined spectrophotometrically by using Uv-Vis spectrophotometer at 574.7 nm. *N,N*-dimethyl-cyclohexylamine/protonated *N,N*-dimethyl-cyclohexylamine carbonate solvent pair was used as switchable solvent in the presented work. The average relative standard deviation was 0.8 % for five repeated determinations having 1.06 µg L^{-1} of Hg (II) concentration. Analytical parameter like limit of detection (LOD), limit of quantification (LOQ) and enhancement factor (EF) were calculated as 0.19 µg L^{-1}, 0.62 µg L^{-1} and 40, respectively. The accuracy of method was evaluated by analyzing NCS ZC81002B human hair certified reference material. The method was successfully applied to determination of mercury in the water and hair samples with satisfactory results.

Keywords: Mercury, Switchable solvent based liquid phase microextraction, Spectrophotometric determination, UV-VIS spectrophotometer, Dithizone.

***Corresponding Author,** E-mail: soylak@erciyes.edu.tr; Fax: +90 352 4374933

1. Introduction

Various natural processes like mineral breakdown, volcanic eruption and soil withering and anthropogenic sources like various industries like catalysis, amalgams, batteries, thermometers, fungicides and pigments are the main cause of natural water pollution with mercury, which is one of the toxic heavy metal [1-3]. Mercury has many chemical and physical form having wide range of properties and also due to its high affinity towards SH group in proteins and lipids tissues, leads to accumulation of mercury that cause cancer and birth defects in superior organisms [4-8]. In natural water mercury exist in three different form; inorganic mercury (Hg^{2+} and its complex form), organic mercury (monomethyl mercury and dimethyl mercury), elemental form (Hg^0) [5]. The permissible limit for mercury in water samples is 10 µg/L as prescribed byWorld Health Organization (WHO). [9, 10] Also, due to amalgam fillings, the concentration of inorganic mercury in blood ranges to 1.3 - 4.3 µg/l, and in urine 1.4 - 4.8 µg/l which cause diverse biological defects [11]. Therefore the determination of inorganic mercury is of immense importance in the natural water bodies [12]. Due to low concentration of mercury in the natural water bodies and high salinity, highly efficient separation and preconcentration methods are required prior to its quantitative determination [13, 14].

Several sophisticated analytical methods have been used for the determination of mercury at trace level which includes cold vapor atomic absorption spectrometry (CVAAS) [15], inductively coupled plasma mass spectrometry (ICP-MS) [16], liquid chromatography coupled with inductively coupled plasma mass spectrometry (LC-ICP-MS) [17] and atomic fluorescence spectrometry (AFS) [18]. But these techniques used for measurement of mercury are expensive and cannot be operated in ordinary laboratory condition. Uv-visible spectrophotometric determination is still a better choice for the determination of mercury in various environmental samples as it has reliable sensitivity, cheap and easy to operate in ordinary laboratory condition [19].

In the recent past different methods have been employed for preconcentration of mercury which include solid phase extraction [20], liquid-liquid phase extraction [21] and cloud point extraction [22, 23]. Due to some disadvantages like time-consuming, expensive, excessive discharge of sample waste and harmful organic solvents into the sink, secondary hazardous material are produced with the procedure that contaminate the environment [24, 25]. Therefore, special attention has to be made for the development of green analytical methods. To achieve the green chemistry approach, novel solvent and equipment systems and reduced liquid phase sample pretreatment techniques “liquid phase microextraction techniques” have been used to extend the concepts and use of green chemistry [26]. In the literature different mode of liquid-liquid microextraction has been reported such as dispersive liquid–liquid microextraction (DLLME) [20], single-drop microextraction (SDME) [27], supramolecular solvent based microextraction (Ss-ME) [28], hollow fiber liquid phase microextraction (HF-LPME) [29] and ionic liquid based microextraction (IL-ME) [30].

Microextraction techniques consist of more than one step; require different polarity of the organic solvents for each step having different solubility in the samples to selectively extract the analyte from matrix components of the sample. The use of different polarity organic solvents for each step of a microextraction technique make these techniques expensive, time consuming and harmful to researchers. Jessop *et at*, has synthesis a new kind of solvent which is called generation “switchable” or “smart” solvents (SS).In switchable solvents, the nonionic liquid becomes an ionic liquid on exposure to atmosphere of carbon dioxide, and then returns to its nonionic form when exposed to nitrogen or add sodium hydroxide. Due to the reversibility of the reaction, the switched solvent can readily be returned to its original state [31, 32].

In order to avoid the use so many organic solvent for single microextraction study, the use of single solvent called switchable-polarity solvents (SPs) are of immense importance. Due to unique properties the switchable-polarity solvents (SPs) are considered as green solvents for a different chemical process like extraction and purification of compounds, chemical synthesis and catalysis reaction due to their reversibly change physical properties abruptly [33, 34].Switchable solvents are liquids that can be reversibly converted from (hydrophilic form in the presence of CO_2 at 1 atm pressure) and (hydrophobic form at the absence of CO_2 after the addition of base). By using polarity switching feature of these solvents the number of extraction solution can be reduced and thus the excessive discharge of organic solvents into the waste can be greatly overcome [35, 36].

The aim of our work was to develop switchable solvent based liquid phase microextraction of mercury from water and hair samples. Switchable solvent was used for preconcentration of mercury for the first time in this work. In this work switching feature of protonated *N,N*-dimethyl cyclohexylamine carbonate-*N,N*-dimethyl cyclohexylamine solvent pair was used for microextraction of mercury. Dithizone was used as chelating agent which form colored complex with mercury which was then selectively extracted by using switchable solvent. The concentration of the complex in extraction phase was measured by using Uv-Visible spectrophotometric at 574.7 nm.

2. Experimental

2.1. Reagents and standards

For the solution preparation water purified with reverse osmosis (18.2 MΩ cm, Millipore) was used. Analytical reagent grade standard of mercury having concentration (1000 mg L^{-1}) was provided by (Charleston, SC, USA) which was used for the preparation of various standard solutions. Dithizone purchased from Riedel-deHaen (Germany) standard solution of 100 mg L^{-1} was prepared by dissolving 0.01 g in 100 mL of methanol (Sigma Aldrich). Different combination of salts and solutions were used to achieve the buffer solution of desired pH. Phosphate buffer solutions (pH 2.0–4.0, sodium dihydrogen phosphate/phosphoric acid), phosphate buffer solutions (pH 5.0-7.0, sodium dihydrogen phosphate/disodium hydrogen phosphate) and ammonia buffer solutions (ammonia-ammonium chloride, pH 8.0-9.0) were used. Triethylamine, *N,N* dimethyl cyclohexylamine, hydrochloric acid (HCl), nitric acid (HNO_3), methanol (CH_3OH) and acetone (C_3H_6O) were also provided by E. Merck (Darmstadt, Germany).

2.2. Instruments

Absorbance measurement were determined by using Hitachi 150-20 spectrophotometer with quartz micro–cell with path length of 10 mm and a volume of 500 µL was used for absorbance measurements. pH adjustment of all the sample solutions were carried out by using pH-meter with, Nel pH 900 (Ankara-Turkey) Model glass-electrode. A centrifuge with centrifugal vials (ALC PK 120 Model, Buckinghamshire, England) was used to achieve quick and complete phase separation. A microwave oven equipped with PTFE vessels, Berghof Speedwave MWS four digestion system (Germany), was used for digestion of hair samples. The digestion program was given in Table 1.

2.3. The synthesis of hydrophilic form of switchable solvent

Protonated *N,N*-dimethyl-cyclohexylamine carbonate switchable extraction solvent was tested as extraction solvent in this microextraction study. Protonated *N,N*-dimethyl-cyclohexylamine carbonate was synthesized by taking 200 mL *N,N*-dimethyl-cyclohexylamine and 200 mL ultrapure water in 1 L glass beaker. After, Dry ice (~ 20 g) as CO_2 supplier was added gradually in the beaker, dissolution of CO_2 was completed and amine phase became cloudy by influence of magnetic stirring. The addition of dry ice was repeated until obtain a single phase, which obtained protonated *N,N*-dimethyl-cyclohexylamine carbonate solution. Afterward, the mixture was stirred for 2 h at room temperature to ensure the complete protonation of *N,N*-dimethyl-cyclohexylamine.

2.4. General procedure

The proposed switchable solvent based liquid phase microextraction (SPS-LPME) was carried out for separation and preconcentration of mercury in 50 mL of centrifuge tube having 10 µg L^{-1} of Hg (II). To the tube, 2 ml of pH 7.0 buffer solution and 12 µg of dithizone were added respectively and allow the solution for 3 min to ensure that the hydrophobic Hg (II)-Dithizone complex formation was complete. A homogenous solution was obtained after the addition of 1.0 mL of protonated *N,N*-dimethyl-cyclohexylamine carbonate. Then, in order to extract the hydrophobic Hg(II)-Dithizone complex, the hydrophilic protonated *N,N*-dimethyl cyclohexylamine was converted into hydrophobic *N,N*-dimethyl-cyclohexylamine (microsized extraction phase) after the addition of 1.5 mL of 10 M NaOH solution. The solution was allowed for 2 min to ensure the formation of *N,N*-dimethyl-cyclohexylamine phase and extraction of Hg (II)-dithizone complex from water phase to in the fine droplets of *N,N*-dimethyl-cyclohexylamine phase. Complete phase separation was achieved by putting the tube inside the centrifuge for 7 min. The aqueous phase was separated and discarded and the extraction phase (*N,N*-dimethyl-cyclohexylamine phase) was diluted to 1 mL using methanol. The concentration of the Hg (II) in last volume was measured quickly to avoid evaporation of methanol at 574.7 nm by using Uv-Visible spectrophotometer. Schematic representation of the developed SPS-LPME steps is presented in the Figure 1.

2.5. Application to real samples

The developed method was applied to the sea water, dam water and dental waste water samples obtained a dental amalgam restorations department in a hospital (Erciyes University, Turkey). Prior to the preconcentration procedure, all the water samples were filtered through a 0.45 m pore size membrane filter to remove suspended particulate matter.

The hair samples and NCS ZC81002B human hair certified reference material were digested in microwave inside a closed Teflon vessel. 100 mg of hair samples or certified reference material were accurately weighed into a PTFE digestion vessel. The decomposition of the samples was carried out in a microwave digestion system. 10 mL of concentrated HNO_3 was added to the vessel and waited for about 20 min before the vessel is closed. A two-step programme was used for digestion of the samples. The extract was transferred into a centrifuge tube and the developed method was applied the extract. Blank experiments were also carried out in the same way.

3. Result and discussion

3.1. Effect of pH

Extraction of the metal ions from polar phase to extraction phase by LPME is greatly influence by the pH of solution. [37, 38] It is because pH of the solution greatly effects the formation of hydrophobic complex Hg-Dithizone. Therefore, the proposed SPS-LPME of mercury was carried out at different pH ranging from 2.0 to 9.0 as shown in the Fig. 2. It can be concluded from the Fig. 2 that quantitative percent recoveries of Hg (II) obtained at the pH range of 5.0-7.0 and reach to its maximum at pH 7.0. Therefore, rests of the other experiment in the presented microextraction method were performed at solution pH of 7.0.

3.2. Selection of switchable extraction solvent

For quantitative recoveries, the selection of suitable switchable solvent is of immense important in SPS-LPME methods. For selection of the appropriate extraction solvent, some properties of the switchable solvent should be kept in mind such as (a) extractive tendency towards the target compounds, (b) must have two forms (hydrophilic and hydrophobic) which are interconvertible by the addition or removal of CO_2 from the solvent system, (c) hydrophobic form of switchable solvent should have low density, (d) high solubility are required for hydrophilic form in water and low solubility required in water for hydrophobic form of switchable solvent so as to established stable two-phase system. Based on these criteria, two switchable solvent triethylamine/protonated triethylamine carbonate and *N,N*-dimethyl-cyclohexylamine/protonated *N,N*-dimethyl-cyclohexylamine carbonate switchable extraction solvent pairs were checked for the extraction of hydrophobic Hg (II)-dithizone complex from sample solution. The recovery valuesobtained for triethylamine/protonated triethylamine carbonate solvent pair is (94±3 %) and the recovery obtained for *N,N*-dimethyl-cyclohexylamine/protonated *N,N*-dimethyl-cyclohexylamine carbonate solvent pair is (99±4%). Both values for two solvent are similar and quantitative. *N,N*-dimethyl-cyclohexylamine/protonated *N,N*-dimethyl-cyclohexylamine carbonate solvent was used for further works.

3.3. Selection of phase transition trigger

Protonated *N,N*-dimethyl-cyclohexylamine (hydrophobic form) and protonated *N,N*-dimethyl-cyclohexylamine carbonate (hydrophilic form) are interconvertible by the addition or removal of CO_2 from the system. In order to remove CO_2 several physical and chemical methods such as addition of sodium hydroxide or hydrochloric acid solution into the solution, passing of inert gas (Ar) in the solution and heating of the solution were checked. No formation of cloudy solution or phase separation was obtained by using of hydrochloric acid solution, heating or passing of inert gas (Ar) ways. Due to high tendency of sodium hydroxide towards protonated hexylamine and tear off hydrogen bond of the amine group, sodium hydroxide gives best result among all the other procedure used. Hence, 10 M sodium hydroxide solution was used as phase transition trigger for this microextraction work.

3.4. Effect of extraction solvent volume

After choosing *N,N*-dimethyl-cyclohexylamine-protonated *N,N*-dimethyl-cyclohexylamine carbonate solvent pair as the best suitable switchable solvent system for this microextraction studies, it was necessary to optimize the volume of protonated *N,N*-dimethyl-cyclohexylamine carbonate, which provide homogenous extraction system for the analyte. The effect of the volume of the protonated *N,N*-dimethyl-cyclohexylamine carbonate as the extraction solvent on the recovery was investigated under fix experimental condition. The microextraction studies were performed at different volume of extraction solution ranging from 0.25 ml to 2.0 mL as shown in the Fig. 3. It can be concluded from the Fig. 3 that there is a gradual increase in the percent recoveries of Hg (II) from 0.25 mL (59 ± 0.8) to 1 mL (96 ± 0.1). Hence, there is no significant change in the percent recoveries there 1.0 mL of protonated *N,N*-dimethyl-cyclohexylamine carbonate was used in further studies.

3.5. Effect of NaOH

As 10 M NaOH was found to be the best phase transition trigger as it remove CO_2 from hydrophilic protonated *N,N*-dimethyl-cyclohexylamine carbonate to form hydrophobic *N,N*-dimethyl-cyclohexylamine. In order to convert the hydrophilic form of switchable solvent to hydrophobic form and also to quantitatively extract the Hg(II)-Dithizone complex from sample solution, the proposed switchable solvent based liquid phase microextraction was carried out at different volume of 10 M of NaOH ranging from 0.25 mL to 2.0 mL as shown in Fig. 4. Results showed that the quantitative recoveries for Hg (II) were obtained between 1.5 and 2.0 mL of 10 M NaOH. In this study, a 1.5 mL of 10 M NaOH was used for further experiments of the proposed method.

3.6. Effect of amount of complexing agent

Selection of the suitable amount of complexing agent (dithizone) is as important as it affect the signals obtained during absorbance measurement in Uv-Visible spectrometry. Dithizone (diphenylthiocarbazone) is known to be one of the effective chelating reagents for metal ions for spectrophotometric determination. [39, 40] Dithizone has been also widely used for the separation and preconcentration of metal ions at trace levels as chelating agent. [41,42] The effect of amount of dithizone as complexing agent was studied in the range of 2-20 µg as shown from Fig. 5. The obtained results indicate that the quantitative recoveries for Hg (II) were obtained in the range of 12 µg to 20 µg of the amount of complexing agent. Therefore 12 µg of dithizone was used in further switchable solvent based liquid-liquid microextraction experiments of Hg (III).

3.7. Effect of sample volume

Determination of preconcentration factor [43-46] is important as it determines the efficiency of the develop method. The highest preconcentration factor of the method can be calculated if the highest sample volume to which the proposed microextraction is successfully applicable is determined. Therefore the proposed switchable solvent based (Ss-LLM) studies were carried out at different volume of samples in the range of 5-50 mL. Quantitative recoveries of Hg (II) were obtained at sample volume below 40 mL, and a preconcentration factor of 40 was using 40 mL sample volume and 1 mL final volume.

3.8. Matrix effect

Due to the complex matrix nature of samples like soil, ore and water, preconcentration methods are greatly influenced [46-49] by various coexisting ions present in the matrices of these samples with analyte metals. Therefore prior to the application of the proposed method to the real samples, the effect of coexisting ions on % recovery of mercury is of immense importance. In order to investigate the effects of matrix ions on SPS-LPME and UV-VIS determination, the proposed microextraction method was carried in the presence of some interfering ions which are coexisting with analyte metal in samples matrices. No interferences were observed from most of the ions tested except for Cu^{2+}, Mn^{2+} and Ni^{2+} ions. To eliminate the interference effects of the ions, the developed SPS-LPME method was carried out in 0.025 M EDTA solution medium as masking agent. The results given in the Table 2 show that there are no significant interferences by these interfering ions even in the presence of high concentration. This shows that the presented method is highly selective and free of interferences.

3.9. Analytical Figures

Analytical performance of the method can be investigated by determining analytical parameters under optimized experimental condition. For one sample, total time is approximately 15 minutes. At the same time, the method could be applied to 20 samples. Calibration standards were subjected to the microextraction procedure. Calibration curve equation was found as A= 0.0053 + 0.040C (A: The absorbance of the solution, C: Determined mercury concentration of the solution). The correlation coefficient (r^2) was 0.989. The linear range for calibration curve is 10-300 μg L^{-1}. The value of limit of detection was found as 0.19 μg L^{-1}, which was calculated as 3 times to the ratio of signal of 10 blank absorbance's/slope of calibration curve, while the value of limit of quantification was found as 0.62 µg L^{-1}, which was calculated as, 10 times to the ratio of signal of 10 blank absorbance's/slope of calibration curve. The relative standard deviations (RSD, %) was calculated as 0.8 % using analysis of five replicates containing 1.06 µg L^{-1} of Hg(II). Both the values of preconcentration factor and enhancement factor were found as 40, which were calculated as (the ratio of the highest sample volume to the eluent volume) and ratio of the Hg(II) concentration in the extraction phase to the initial concentration of Hg(II) in the sample solution respectively.

3.10. Applications

The validation of the presented SPS-LPME method was checked by the analyzing NCS ZC81002B human hair certified reference material. For the analysis of mercury content of certified reference material, 5 mL of 0.05 M EDTA was used as masking agent in the microextraction procedure. While the certified value of NCS ZC81002B human hair certified reference material was 1.06±0.28 µg g^{-1}, the mercury level was found 1.02±0.24 µg g^{-1} (N=3). The recovery values were 96%. It was found that there was no significant difference between the result obtained and the certified result. The proposed method can successfully applied for quantitative determination of Hg (II) at trace level in real samples.

For the addition-recovery applications, the proposed SPS-LPME method was applied to three water samples (Sea water, Dam water, dental waste water) and two hair samples (Hair I and Hair II) and the results are given in Table 3. The quantitative % recoveries results obtained shows that the developed SPS-LPME is sensitive, precise and accurate for the determination of Hg (II) in real samples.

The developed SPS-LPME method was compared for its extraction efficiency with other microextraction methods regarding LOD, preconcentration factor and the results are given in Table 4. It can be concluded from the Table 4 that the presented method is generally either comparable or more efficient than the other microextraction method in the literature. [54-61]

4. Conclusion

A green approach towards the preconcentration and determination of Hg (II) in water and hair samples was achieved by using switchable solvent based liquid phase microextraction (SPS-LPME) associated with Uv-Vis spectrophotometric determination. The method is highly environmental friendly as low organic wastes are produced due to the use of switchable solvent. Low value of LOD of 0.19 $\mu g\ L^{-1}$ and LOQ of 0.62 $\mu g\ L^{-1}$ reflects high sensitivity of the method. Preconcentration factor (PF) and enhancement factor (EF) each having value of 40 shows that the method is highly efficient. The method is also cost effective because, there is no need of special laboratory equipment's. The proposed method is comparable or more than the other preconcentration method regarding LOD. The method was successfully applied to water and hair samples.

Acknowledgement

Mansoor Khan is thankful to the Scientific and Technological Research Council of Turkey (TUBITAK) under “2216 Research Fellowship Programme for Foreign Citizens” for financial support.

References

1 M. Gharehbaghi, F. Shemirani, M. Baghdadi, Int. J. Environ. Anal. Chem. 2009, **89,** 21-33.

2 A. Afkhami, T. Madrakian, H. Siampour, Int. J. Environ. Anal. Chem. 2006, **86,** 1165-1173.

3 M. Zaki, M. Esmaile, Anal. Lett. 1997, **30,** 1579-1590.

4 F. Pena-Pereira, I. Lavilla, C. Bendicho, L. Vidal, A. Canals, Talanta, 2009, **78,** 537-541.

5 K. Leopold, M. Foulkes, P. Worsfold, Anal. Chim. Acta, 2010, **663,** 127-138.

6 E.M. Martinis, P. Bertón, R.A. Olsina, J.C. Altamirano, R.G. Wuilloud, J. Hazard. Mater. 2009, **167,** 475-481.

7 A. Abdollahi, M. Amirkavehei, M.M. Gheisari, F. Tadayon, E3S Web of Conferences, EDP Sci. 2013, pp. 41006.

8 M. Tuzen, A. Sari, D. Mendil, M. Soylak, J. Hazard. Mater. 2009, **169**, 263-270.

9 World Health Organisation. Guidelines for Drinking Water Quality; World Health Organization: Geneva, Switzerland, 2008.

10 S.J. Cobbina, A.B. Duwiejuah, R. Quansah, S. Obiri, N. Bakobie, Int. J. Environ. Res. Public Health 2015, **12,** 10620-10634

11 J.S. Vamnes, R. Eide, R. Isrenn, P.J. Höl, N.R. Gjerdet, Sci. Total Environ. 2003, **308,** 63-71.

12 M. Tuzen, M. Soylak, Bull. Environ. Contam. Toxicol. 2005, **74**, 968-972.

13 M. Kawaguchi, K. Inoue, M. Yoshimura, R. Ito, N. Sakui, N. Okanouchi, H. Nakazawa, J. Chromatogr. B, 2004, **805**, 41-48.

14 H. Ashkenani, S. Dadfarnia, A.M.H. Shabani, A.A. Jaffari, A. Behjat, J. Hazard. Mater. 2009, **161,** 276-280.

15 M. Tuzen, I. Karaman, D. Citak, M. Soylak, Food Chem. Toxicol. 2009, **47,** 1648-1652.

16 E.V. Alonso, M.S. Cordero, A.G. de Torres, P.C. Rudner, J.C. Pavón, Talanta, 2008, **77,** 53-59.

17 L.H. Reyes, G.M. Rahman, H.S. Kingston, Anal. Chim. Acta, 2009, **631,** 121-128.

18 V.N. Tirtom, Ş. Goulding, E. Henden, Talanta, 2008, **76**, 1212-1217.

19 F. Théraulaz, O.P. Thomas, Microchim. Acta, 2008, **113,** 53-59.

20 J.P. Snell, W. Frech, Y. Thomassen, Analyst, 1996, **121**, 1055-1060.

21 X. Jia, Y. Han, X. Liu, T. Duan, H. Chen, Spectrochim. Acta Part B: At. Spectrosco. 2011, **66**, 88-92.

22 C.-G. Yuan, K. Lin, A. Chang, Microchim. Acta, 2010, **171,** 313-319.

23 Y. Li, B. Hu, Spectrochim. Acta B, 2007, **62,** 1153-1160.

24 M. Soylak, E. Yilmaz, At. Spectrosc. 2013, **34**, 15-19.

25 Z.A. Alothman, E. Yilmaz, M. Habila, A. Shabaka, M. Soylak, Microchim. Acta, 2013 **180,** 669-674.

26 L. Xia, X. Li, Y. Wu, B. Hu, R. Chen, Spectrochim. Acta Part B: At. Spectrosco. 2008, **63**, 1290-1296.

27 H. Bagheri, M. Naderi, J. Hazard. Mater. 2009, **165**, 353-358.

28 Y. He, Chem. Pap. 2014, **68**, 995-1007.

29 A. Spietelun, Ł. Marcinkowski, M. de la Guardia, J. Namieśnik, Talanta, 2014, **119,** 34-45.

30 S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Spectrochim. Acta B 2009, **64**, 666-671.

31 E. Yilmaz, M. Soylak, Anal. Chim. Acta, 2015, **886**, 75-82.

32 E. Yilmaz, M. Soylak, J. Anal. At. Spectrom. 2015, **30,** 1629-1635.

33 P.G. Jessop, D.J. Heldebrant, X. Li, C.A. Eckert, C.L. Liotta, Nature, 2005, **436**, 1102-1102.

34 J.R. Vanderveen, J. Durelle, P.G. Jessop, Green Chem. 2014, **16**, 1187-1197.

35 Y. Liu, P.G. Jessop, M. Cunningham, C.A. Eckert, C.L. Liotta, Science, 2005, **313**, 958-960.

36 I. Anugwom, P. Mäki-Arvela, P. Virtanen, S. Willför, R. Sjöholm, J.-P. Mikkola, Carbohydr. Polym. 2012, **87,** 2005-2011.

37 K. Pytlakowska, Microchim. Acta 2016, **183,** 91–99.

38 M. Tuzen, M. Soylak, J. Hazard. Mater. 2009, **162,** 724-729.

39 C.R. Weast (Editor), CRC Handbook of Chemistry and Physics, CRC Press, Ohio, 1976

40 J. Chwastowska, E. Kosiarska, Talanta, 35 (1988) 439.

41 M. Hiraide, M.H. Sorouradin, H. Kawaguchi, Anal. Sci. 10 (1994) 125.

42 A. Uzawa, W. Yoshimura, T. Okutani, Bunseki Kagaku, 44 (1995) 391.

43 M. Bagtash, Y. Yamini, E. Tahmaseb, J. Zolgharnein, Z. Dalirnasab, Microchim Acta 2016, **183,** 449–456.

44 M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerozohori, A. Khanmohammadi, M. Soylak, J. Hazard. Mater. 2008, **152**, 1248-1255.

45 O.S. Taskin, N. Ersoy, A. Aksu, B. Kiskan, N. Balkis, Y. Yagci, Polymer Int. 2016, DOI: 10.1002/pi.5074

46 M. Soylak, O. Ercan, J. Hazard. Mater. 2009, **168,** 1527-1531.

47 M. Soylak, L. Elci, M. Dogan, , Anal.l Lett. 1993, **26,** 1997-2007.

48 H. Shirkhanloo, M. Falahnejad, H.Z. Mousavi, J. Appl. Spectrosc. 2016**, 82,** 1072-1077.

49 D. Trak, E. Kendüzler, Y. Arslan, Anal. Lett. 2016, doi:10.1080/00032719.2015.1113424

50 C. Huang, B. Hu, Spectrochim. Acta 63B, 2008, **63**, 437-444.

51 C. Zheng, Y. Li, Y. He, Q. Ma, X. Hou, J. Anal. At. Spectrom. 2005, **20,** 746-750.

52 M.E. Mahmoud, Anal. Chim. Acta, 1999, **398**, 297-304.

53 J.C. Wuilloud, R.G. Wuilloud, M.a.F. Silva, R.A. Olsina, L.D. Martinez, Spectrochim. Acta 2002, **57B,** 365-374.

54 N. Rajesh, M.S. Hari, Spectrochim. Acta, 2008, **70A**, 1104–1108.

55 Z. Li, S. Xia, J. Wang, C. Bian, J. TongState, J. Hazard. Mater., 2016, **301**, 206–213.

56 H.I. Ulusoy, J. AOAC Int., 2014, **97,** 238-244.

57 V.A. Lemos, L.O. dos Santos, E.D. Silva, J. AOAC Int., 2012, **95**, 227-231,

58 R. Gurkan, T. Cepken, H.I. Ulusoy, Turk J. Chem., 2012, **36**, 159-177.

59 H.I. Ulusoy, R. Gurkan, S. Ulusoy, Talanta, 2012, **88**, 516– 523

60 E. Beceiro-Gonzalez, A. Guimaraes, M. Alpendurada, J. Chromatogr. A, 2009, **1216,** 5563-5569.

61 Z. Gao, X. Ma, Anal. Chim. Acta, 2011, **702**, 50-55.

Table 1. The microwave digestion program for hair samples

Step	Program 1	Program 2
T (°C)	145	190
P (bar)	50	50
Power (%)	70	90
Ta (min)	10	5
Time (min)	5	10

Table 2. Effect of some co-existing ions on extraction efficiency of Hg(II) (Experimental conditions; pH: 7.0, volume of extraction solution: 1.0 mL, amount of dithizone: 12 µg, volume of 10 M NaOH solution: 1.5 mL, sample volume: 10 mL, volume of 0.05 M EDTA: 5 mL (N=3).

Matrix ion	**Amount added (µg)**	**Added as**	**% Recovery**
Na^+	5000	$NaNO_3$	95±2
K^+	5000	KCl	98±1
Ca^{2+}	500	$Ca(NO_3)_2.4H_2O$	94±2
Mg^{2+}	500	$Mg(NO_3)_2.6H_2O$	97±1
Zn^{2+}	10	$Zn(NO_3)_2.7H_20$	103±3
Cd^{2+}	5	$Cd(NO_3)_2.6H_2O$	103±5
Pb^{2+}	5	$Pb(NO_3).6H_2O$	99±3
Cu^{2+}	2.5	$Cu(NO_3).6H_2O$	97±5
Ni^{2+}	2.5	$Ni(NO_3)_2.6H_2O$	97±4
Co^{2+}	5	$Co(NO_3)_2.6H_2O$	100±3
Mn^{2+}	2.5	$Mn(NO_3)_2.4H_2O$	102±3
SO_4^{2-}	1000	Na_2SO_4	101±3
CO_3^{2-}	500	Na_2CO_3	95±1
F^-	1000	NaF	96±3

[a] Mean ± standard deviation.

Table 3. Addition and recovery test for SPS-LPME of mercury in water and hair samples (Experimental conditions; pH: 7, P-TEA-BC volume: 1.0 mL, amount of dithizone: 12 µg, volume of 10 M NaOH solution: 1.5 mL, sample volume 10 mL, volume of 0.05 M EDTA: 5 mL (N=3).

Sample	Added, µg	Found, µg	Recovery, %
Sea water	0	0.95±0.02[a]	-
	5	5.73±0.03	96
	6	6.67±0.06	95
Dam Water	0	BDL	-
	3	3.00±0.05	100
	6	6.29±0.06	105
Waste Water	0	2.33±0.05	-
	5	7.43±0.05	102
	8	10.4±0.03	101
Hair I	0	BDL	---
	1	1.04±0.10	104
	2	2.02±0.05	102
Hair II	0	BDL	---
	2	1.90±0.30	95
	3	2.87±0.08	96

[a] Mean ± Standard deviation.

[b] BDL: Below detection limit.

Table 4. Comparison of the presented method with other methods for the determination of Hg (II)

Method	Analysis	PF/EF[a]	Detection Limit μg L^{-1}	Sample	Ref.
Ionic liquid phase microextraction	UV-Vis	50	18.8	Water	[1]
Solid phase extraction	ICP-MS	--	0.06	Biological	[50]
Liquid-liquid extraction	Fluorometric	--	0.2	Water	[51]
Solid phase extraction	Uv-Vis	--	0.05	Water	[52]
Cloud point extraction	ICP-MS	100	0.04	Water	[53]
Solid phase extraction	spectrophotometry	33	2.0	water	[54]
ionic liquids microextraction	Stripping voltammetry	17	0.05	water	[55]
micelle-mediated extraction	spectrophotometry	33.3	0.86	water	[56]
dispersive liquid liquid microextraction	spectrophotometry	64	3.3	water	[57]
Surfactant-sensitized	spectrophotometry	-	6	water	[58]
Cloud point extraction	spectrophotometry	33.3	1.65	water	[59]
Switchable solvent based liquid phase microextraction	spectrophotometry	40	0.19	Water, hair	This study

[a] Preconcentration factor/enhancement factor

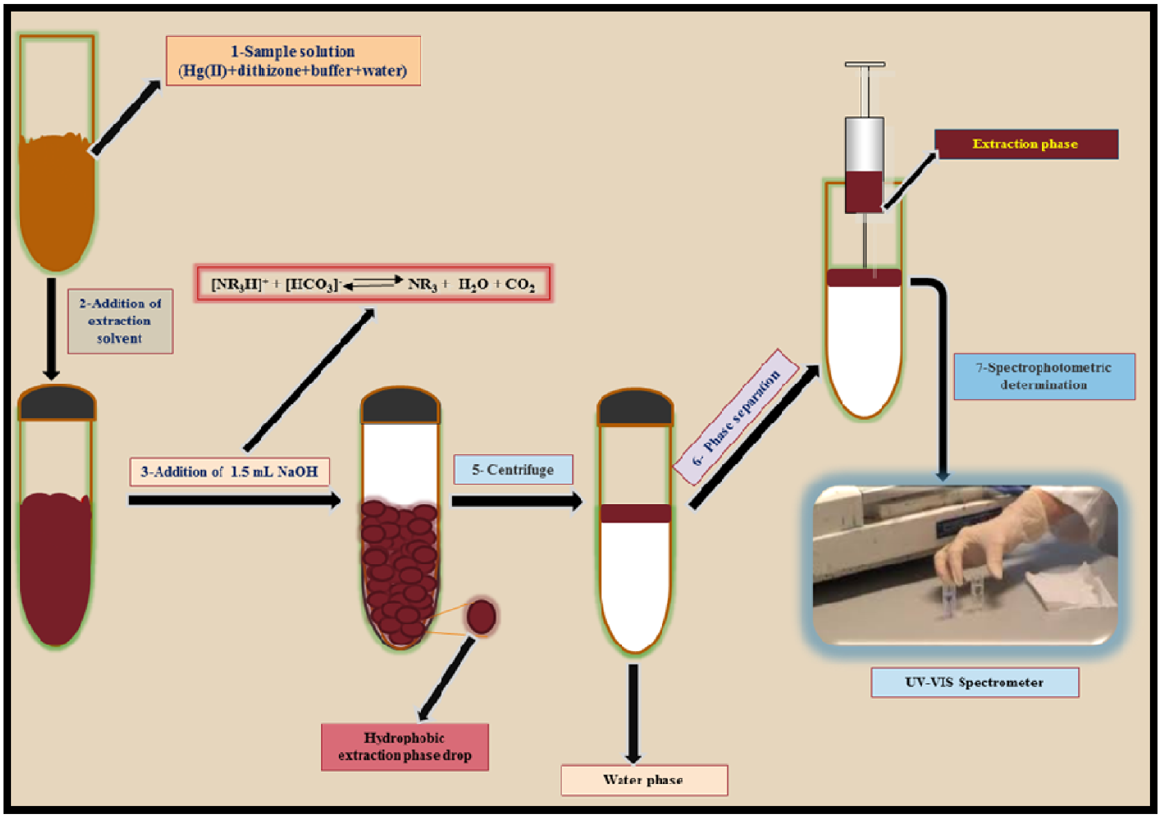

1-Sample solution
(Hg(II)+dithizone+buffer+water)
2-Addition of extraction solvent
$[NR_3H]^+ + [HCO_3]^- \rightleftharpoons NR_3 + H_2O + CO_2$
3-Addition of 1.5 mL NaOH
Hydrophobic extraction phase drop
5- Centrifuge
Water phase
6- Phase separation
Extraction phase
7-Spectrophotometric determination
UV-VIS Spectrometer

Fig. 1

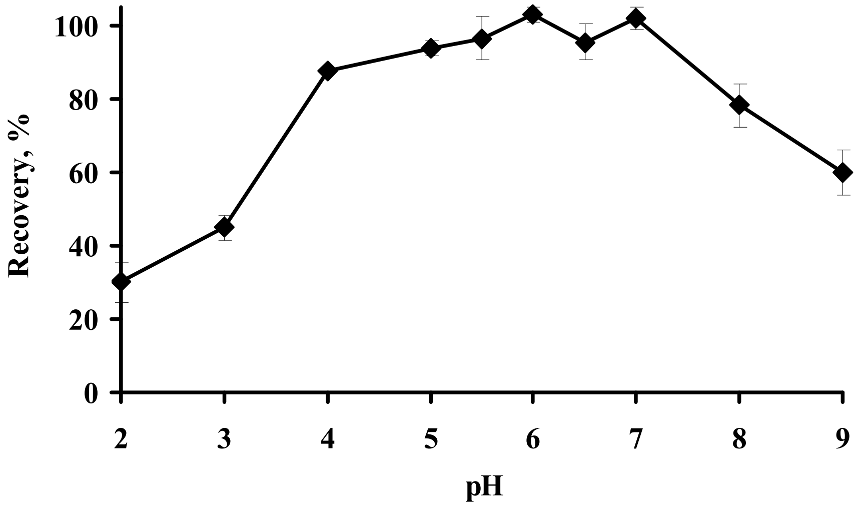


Fig. 2

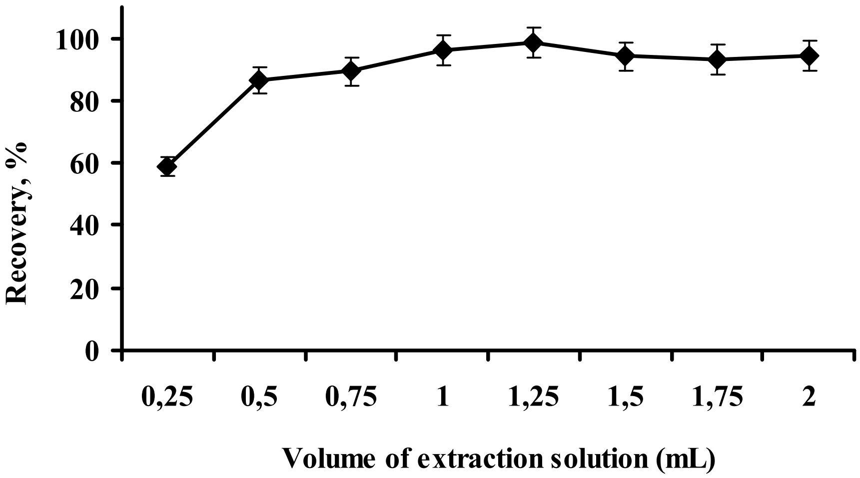

100
80
60
40
20
0
Recovery, %
0,25
0,5
0,75
1
1,25
1,5
1,75
2
Volume of extraction solution (mL)

Fig. 3

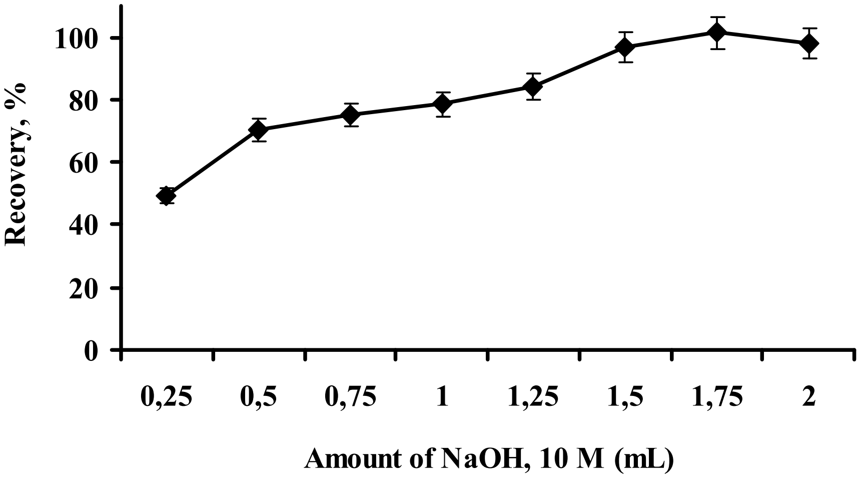

Recovery, %
0
20
40
60
80
100
0,25
0,5
0,75
1
1,25
1,5
1,75
2
Amount of NaOH, 10 M (mL)

Fig. 4

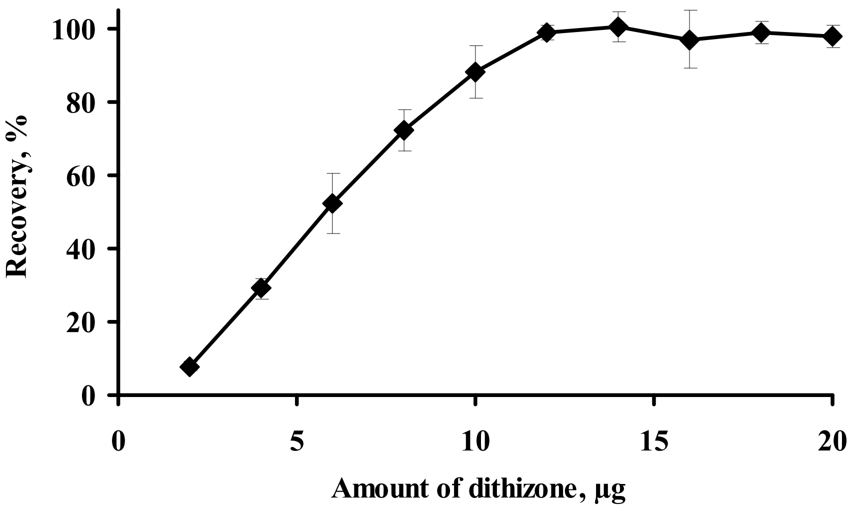


Fig. 5

Switchable solvent based liquid phase microextraction of mercury from environmental samples: A green aspect

Mansoor Khan [1, 2], **Mustafa Soylak**[1*]

[1] Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri-TURKEY

[2] Institute of Chemical Sciences, University of Peshawar, Peshawar-Pakistan