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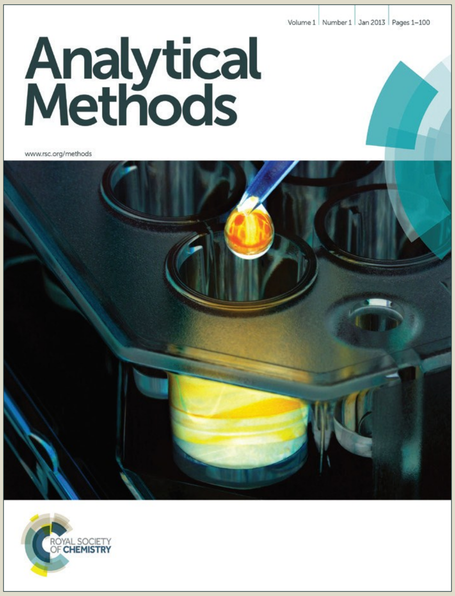

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A green, novel and simple microprecipitation technique for separation and preconcentration of cadmium with 1-(2-thiazolylazo)-2-naphthol in food samples and determination by microsampling flame atomic absorption spectrometry

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Abstract

A microprecipitation technique is developed based on the application of Cd(II)-1-(2-thiazolylazo)-2-naphthol (TAN) precipitate from aqueous solution and, at the same time, to help in the accumulation and aggregation of the complex to obtain a solid phase of separable particles. This condition facilitates phase separation, and the aqueous phase can be removed with a syringe, while the remaining solid particles are dissolved in concentrated nitric acid and introduced to a flame atomic absorption spectrometer using a microinjection system for Cd(II) determination. Quantitative recovery values for cadmium were obtained at pH 8. The method offered a limit of detection (LOD) of 0.25 μg L^{-1}, a limit of quantification (LOQ) of 0.83 μg L^{-1} and a relative standard deviation (RSD) of 5.5%. The procedure was validated by addition/recovery tests and by applying bovine liver certified reference materials. The method was successfully applied for the preconcentration and determination of cadmium in food samples.

Keywords: Cadmium, 1-(2-Thiazolylazo)-2-naphthol, microprecipitation, flame atomic absorption spectrometry.

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1. Introduction

Among the heavy metals, cadmium is considered to be the most serious and health hazardous element. It is reported to be carcinogenic in human organs. Its existence in the environment has increased in the last century due to human activities. It is used in nickel–cadmium batteries, in paint pigments, and in preparing polyvinyl chloride plastics. It may be transferred over a long distance by the atmosphere from emission sources and accumulated through the food chain, ending up in a human body.[1-5] Consumption of contaminated food is the main source for human exposure to cadmium.[6] Cadmium targets the human kidney and leads to renal tubular dysfunction.[7] In addition, high exposure to cadmium disturbs the calcium cycle in the human body and may cause kidney stones.[7-9] Therefore, it is important to monitor and accurately determine cadmium in environmental samples. However, for this purpose, Flame Atomic Absorption Spectrometry (FAAS) is not suitable because of the trace levels of cadmium in some samples as well as matrix interference.[10] Sample pretreatments are used to overcome this limitation. There are many techniques used for sample pretreatment, such as Solid Phase Extraction (SPE),[11] Dispersive Liquid-Liquid Microextraction (DLLME),[12] Cloud Point Extraction (CPE),[13] Chemical Precipitation (CP),[14] and Ligandless Cloud Point Extraction (LCPE).[15] Nekoueia and Nekouei have been determined cadmium concentrations by a UV-Vis spectrophotometric method after preconcentration using the CPE method based on Mixed-Micelle Mediated Extraction (MMME) and ion association.[16] Using this method, the results showed a limit of detection (LOD) of 4.05 µg L^{-1}. Shahtaheri et al. reported the determination of cadmium after preconcentration using SPE, which exhibited a recovery of not less than 92%.[17] Asci et al. developed a method for the determination of cadmium in oils by SPE using zinc as an adsorbent.[18] Kartikeyan et al. developed a procedure for the determination of cadmium based on on-line preconcentration using a C18 column.[19] Väisänen and Suontamo reported an extraction procedure for cadmium based on ultrasound-assisted aqua regia extracts, which exhibited a LOD of 0.04 µg L^{-1}.[20] Jafarvand and Shemirani[21] introduced a procedure for the determination of cadmium based on supramolecular-enhanced, dispersive liquid–liquid microextraction (SM-DLLME), which exhibited a LOD of 0.3 µg L^{-1}. However, research is still continuing on how to reduce solvent usage during sample pretreatment.[22,23]

Therefore, this work aimed to develop an microprecipitation procedure based on using cadmium(II)-1-(2-thiazolylazo)-2-naphthol precipitate and accumulate to form separable solid parts in the sample solution. The e method was applied to the preconcentration and separation of cadmium from food samples.

2. Experimental

2.1. Chemicals and instruments

The chemicals used in this work were analytical grade. A Millipore Milli-Q system was used to prepare the distilled and deionized water. Standard solutions of Cd(II) (1000 mg L^{-1}) were prepared by dissolving the nitrate salt (Merck) in water. The working standard solutions were prepared daily using dilutions of a stock standard solution. The 0.1 % (w/v) solution of 1-(2-thiazolylazo)-2-naphthol (TAN) was provided by dissolving suitable amount of TAN (Merck, Darmstadt, Germany) in 100 mL of ethanol/water (1/1 v/v). Buffer solutions were prepared according to literatures. [23, 24]

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) including an air–acetylene flame and a hollow cathode lamp was used to measure concentrations of cadmium. The instrumental parameters were adjusted as recommended by the manufacturer. A homemade microsample injection system coupled to the nebulizer needle using a PTFE capillary tube (length of 10 cm) attached with a Teflon funnel (capacity 20–200 μL) was used. The extractant phase was injected into this system. The absorbance signal was measured according to the peak height in the continuous aspiration mode.[24, 25] The reading time was 2 second.

A Nel pH-900 (Ankara, Turkey) and a Metrohm pH meter (model 691, Switzerland) with a combined glass electrode were used for the pH measurements. An ALC PK 120 Model centrifuge (Buckinghamshire, England) was used during the centrifugation processes.

2.2. Test procedure

The procedure of microprecipitation technique is described in Figure 1. In detail, 30 mL of a solution containing Cd(II) was placed in a 50-mL centrifuge tube, then 5 mL of ammonia buffer was added, and the pH of the sample solution was adjusted to 8.0 using dilute NaOH and HCl solutions. Then, 200 μL of 0.1% 1-(2-thiazolylazo)-2-naphthol (TAN) was added to the sample. The mixture was left for 15 min to allow for complex and precipitate formation and accumulation into a separable solid phase. The aqueous solution was removed by syringe, and the remaining solid phase was then dissolved in concentrated nitric acid, to give a final total volume of 750 μL. Finally, 50 μL of the solution was introduced into the FAAS nebulizer using a microinjection system to measure the cadmium concentration.

2.3. Application to real samples

Food samples, including chili powder, black pepper, thyme, hemp, black cumin, cuminum cyminum, cinnamomum verum and alpinia officinarum, as well as bovine liver certified reference materials, were digested as described in the literature.[24] The food samples were collected from markets in Riyadh, Saudi Arabia and Kayseri, Turkey. The samples were dried at 80 °C and homogenized using an agate homogenizer. Then, 0.5 g of each sample was placed into a beaker. Concentrated nitric acid (15 mL) was added to the beakers, and the beakers were heated on a hot plate at 100 °C to dryness. The remains in the beakers were cooled, 10 mL of concentrated HNO_3 and 5 mL of H_2O_2 were further added, and the beakers were heated to dryness. The mixture was dissolved in water and filtered. The procedure given in the test section was then followed for each sample.

3. Results and discussions

3.1. Effect of pH

Complex formation between metal ions and ligands is significantly affected by the pH of the solution; therefore, the recovery % varied depending on the pH.[26,29] In the present work, the pH of the Cd(II) solution was examined in a pH range from 2 to 9. The results are presented in Fig. 2. It is clear from the figure that the recovery % increases when increasing the pH from 2 to 7.5, and after this, at pH 9, it decreases. Quantitative recoveries were obtained at the pH range of 7.5-8.5. This may be due to the suitability of the pH 8 medium for the maximum interaction between Cd(II) and 1-(2-thiazolylazo)-2-naphthol, giving the maximum recovery %. Therefore, pH 8 was selected for further experiments.

3.2. Effect of the amount of 1-(2-thiazolylazo)-2-naphthol

The proposed procedure is based on using 1-(2-thiazolylazo)-2-naphthol (TAN) ligand for two purposes; the first one is to chelate Cd(II) from the sample solution, and the second is to help accumulation of the complex to obtain solid separable particles. This condition facilitates the removal of the aqueous phase using a syringe. Therefore, the amount of 1-(2-thiazolylazo)-2-naphthol is critical for obtaining a quantitative recovery and should be optimized. Herein, a volume of 0.1% 1-(2-thiazolylazo)-2-naphthol was studied in the range of 50 to 300 µL. The results presented in Fig. 3 reveal that 200 µL is suitable for quantitative recovery at pH 8.

3.3. Effect of coexisting cations and anions

To evaluate the procedure and its capacity to retain quantitative recovery under different sample conditions, it is important to determine the effect of the presence of coexisting ions.[30-37] Herein, the effects of the presence of Na^+, K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Cl^-, CO_3^{2-}, NO_3^-, SO_4^{2-} and F^- were investigated. The results are presented in Table 1. It can be concluded from the Table 1 that the proposed method is matrix independent and can be applied to samples with a different matrix.

3.4. Effect of sample volume

Sample volume is a critical factor for the development of an extraction technique because the preconcentration factor is directly proportional to it.[38-43] The recommended extraction procedure is that with a high preconcentration factor because of increased sensitivity. Herein, the effect of sample volume on the recovery % was tested in the range of 10 mL to 45 mL. The results in Fig. 4 showed that a quantitative recovery can be attained up to 30 mL. Therefore, the preconcentration factor was calculated as 40 depending on the final volume for an injection of 750 μL.

3.5. Analytical features

Addition/recovery tests were conducted to evaluate the proposed method. Known concentrations of Cd(II) were spiked into the sample solutions, and the recovery % values were calculated. The results are presented in Table 2, which reveals the accuracy of the proposed method. In addition, the SRM 1577b bovine liver certified reference material was analyzed for preconcentration and determination of Cd(II), and the recovered value is compared with the certified value. The results presented in Table 3 show that there is no significant difference between the achieved result and the certified content.

The limit of detection (LOD), calculated based on seven determinations of the standard deviation in the blank, was 0.25 μg L^{-1}. The limit of quantification (LOQ), calculated as three times the LOD, was 0.83 μg L^{-1}. The relative standard deviation (RSD) determined from seven analyses of the standard solution of Cd(II) (20 μg L^{-1}) was 5.5 %.

Table 4 presents a comparison between the proposed method and other methods from a literature survey. It can be observed from the table that the proposed method is comparable and possess a high efficiency for cadmium determination.

3.6. Application to real samples

The main source of human exposure to Cd(II) is consuming contaminated food.[6] Therefore, in the present study, food samples, including chili powder, black pepper, thyme, hemp, black cumin, cuminum cyminum, cinnamomum verum and alpinia officinarum, were analyzed for Cd(II) determination. The results are presented in Table 5, which reveals the suitability of the proposed procedure for real sample applications.

4. Conclusions

The proposed method showed quantitative recovery of Cd(II) at pH 8 without the presence of any dispersive or extraction solvents. This savings in solvent usage will enhance environmental safety by decreasing extraneous solvent as well as, from an economic view, reduce the analysis cost. A quantitative recovery can be attained in a sample up to a volume of 30 mL. The proposed procedure is matrix independent, and the developed method showed a high efficiency compared with others from the literature.

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References

1. K. Kadirvelu and C. Namasivayam, Environ. Technol., 2000, **21**, 1091.
2. M. Ghaedi, F. Marahel, A. Shokrollahi, M. Montazerozohori and M. Soylak, Quim. Nova., 2010, **33,** 404.
3. S.J. Nagourney, M. Heit and D. C. Bogen, Talanta, 1987, **34**, 465.
4. Y.M. Abd-Elhakim, N.I. El Sharkawy and G.G. Moustafa, J. Vet. Diagn. Invest., 2016, **28,** 70.
5. R. Saraymen, M. Soylak and I. Narin, Fresen. Environ. Bull., 1998, **7**, 403.
6. K. Kadirvelu and C. Namasivayam, Environ. Technol., 2000, **21**, 1091.
7. L. Bat, H.C. Oztekin and F. Ustun, Turk. J. Fish. Aquat. Sc., 2015, **15,** 393.

8. A. Bernard, Indian J. Med. Res., 2008, **128**, 557.
9. S. Kempton, R. M. Sterritt and J. N. Lester, Talanta, 1982, **29**, 675.
10. A. Vural, Bull. Mineral Res. Exploration, 2014, **148,** 85.
11. M. Habila, E. Yilmaz, Z. A. ALOthman and M. Soylak, J. Ind. Eng. Chem., 2014, **20** 3989.
12. Z. A. ALOthman, M. Habila, E. Yilmaz and M. Soylak, J. AOAC Int., 2013, **96**, 1425.
13. J. Chen and K. C. Teo, Anal. Chim. Acta., 2001, **450**, 215.
14. M. M. Matlock, B. S. Howerton and D. A. Atwood, Water Res., 2002, **36**, 4757.
15. S. Candir, I. Narin and M. Soylak, Talanta, 2008, **77**, 289.
16. F. Nekoueia and S. Nekouei, Indian J. Sci. Res., 2014, **8**, 130.
17. S. J. Shahtaheri, M. Khadem, F. Golbabaei and A. R. Froushani, Iran. J. Environ. Health. Sci. Eng., 2006, **3**, 45.
18. M. Y. Asci, A. Efendioglu and B. Bati, Turk J. Chem., 2008, **32**, 431.
19. S. Kartikeyan , B. Vijayalekshmy, S. Chandramouleeswaran, T. P. Rao and C. S. P. Iyer, Anal. Lett., 1997, **30**, 1037.
20. A. Väisänen and R. Suontamo, J. Anal. At. Spectrom., 2002, **17**, 739.
21. S. Jafarvand and F. Shemirani, Anal. Methods, 2011, **3**, 1552.
22. K. Pilaniya, H. K. Chandrawanshi, U. Pilaniya, P. Manchandani, P. Jain and N. Singh, J. Adv. Pharm. Technol. Res., 2010, **1**, 302.
23. M. Habila, Z. A. ALOthman and M. Soylak, RSC Adv., 2014, **4,** 55610.
24. M. Soylak and E. Yilmaz, Desalination, 2011, **275**, 297.
25. S. R. Yousefi and F. Shemirani, Anal. Chim. Acta, 2010, **669**, 25.
26. Z. A. Alothman, M. Habila, E. Yilmaz and M. Soylak, Atom. Spectrosc., 2013, **34**, 175.
27. Z. A. Alothman, E. Yilmaz, M. Habila and M. Soylak, Desalin. Water Treat., 2013, **51**, 6670.

28. X. Song, J. Li, C. Liao and L. Chen, Chromatographia, 2011, **74**, 89.

29. Z. A. Alothman, Y. E. Unsal, M. Habila, M. Tuzen and M. Soylak, Desalin. Water Treat., 2015, **53**, 3457.

30. Z. A. Alothman, M. A. Habila, E. Yilmaz and M. Soylak, Microchim. Acta., 2012, **177** 397.

31. H. B. Senturk, A. Gundogdu, V. N. Bulut, C. Duran, M. Soylak, L. Elci and M. Tufekci, J. Hazard. Mater., 2007, **149**, 317.

32. S. Nekouei, Chemia, 2014, **59**, 49.

33. F. A. Aydin and M. Soylak, Talanta, 2007, **72**, 187.

34. O.M. Kalfa, O. Yalcinkaya and A.R. Turker, Turk. J. Chem. 2012, **36**, 885.

35. D. Mendil, M. Tuzen and M. Soylak, J. Hazard. Mater., 2008, **152,** 1171.

36. H. Eskandari, Turk. J. Chem. 2012, **36,** 631.

37. M. Tuzen, M. Soylak, D. Citak, H.S. Ferreira, M.G.A. Korn and M.A. Bezerra, J. Hazard. Mater., 2009, **162,** 1041.

38. M. Ataee, T. Ahmadi-Jouibari and N. Fattahi, Int. J. Environ. An. Ch., 2016, **96,** 271.

39. S.G. Ozcan, N. Satiroglu and M. Soylak, Food Chemical Toxicol., 2010, 48, 2401.

40. H. Peng, N. Zhang, M. He, B. Chen and B. Hu, Int. J. Environ. An. Ch., 2016, **96,** 212.

41. M. Tuzen and M. Soylak, J. Hazard. Mater., 162, 724-729 (2009).

42. H. Bagheri, A.A. Asgharinezhad and H. Ebrahimzadeh, Food Anal. Methods, 2016, **9,** 876.

43. M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerozohori, A. Khanmohammadi and M. Soylak, J. Hazard. Mater., 2008, **152,** 1248.

Figure Captions

Figure 1. The microprecipitation procedure for preconcentration of cadmium

Figure 2. Effect of the pH on the recovery of Cd(II) (N=3).

Figure 3. Effect of the amount of 1-(2-thiazolylazo)-2-naphthol on the recovery of Cd(II) (N=3).

Figure 4. Effect of sample volume on the recovery of Cd(II) (N=3).

Table 1. Effect of coexisting ions on the recovery of Cd(II) (N=3).

Ions	Concentration (mg/L)	Added As	Recovery, %
K^+	2000	KCl	95±3
Na^+	8000	NaCl	95±3
Mg^{2+}	200	$Mg(NO_3)_2$. $6H_2O$	90±3
Ca^{2+}	200	$CaCl_2$	93±1
Co^{2+}	10	$Co(NO_3)_2.6H_2O$	94±3
Ni^{2+}	10	$Ni\ (NO_3)_2.6H_2O$	93±5
Cu^{2+}	10	$Cu(NO_3)_2.3H_2O$	98±3
Fe^{3+}	10	$Fe(NO_3)_3.9H_2O$	94±3
Zn^{2+}	10	$Zn(NO_3)_2$	100±2
SO_4^{2-}	200	Na_2SO_4	94±4
F^-	200	NaF	95±6
CO_3^{2-}	1000	$Na_2\,CO_3$	98±4
NO_3^-	1000	KNO_3	93±2
Cl^-	8000	NaCl	95±3

Table 2. Addition/recovery investigation for Cd(II) from pepper sample (N=5).

Added, µg g^{-1}	Found, µg g^{-1}	Recovery, %
0	0	-
3.00	2.98±0.04	99±1
6.00	5.94±0.06	99±1

Table 3. Validation of the proposed procedure using bovine liver certified reference material (N=5).

Certified value, µg g^{-1}	**Found value, µg g^{-1}**	**Recovery, %**
0.5	0.48 ± 0.02	97±4

Table 4. Comparison between the proposed procedure and other methods from literature for cadmium preconcentration

Method	LOD (μg L^{-1})	Ref.
Solid Phase Extraction (SPE)	0.15	[11]
Cloud Point Extraction (CPE)	4.05	[16]
Solid Phase Extraction (SPE)	28.0	[19]
Ultrasound-assisted aqua regia	0.04	[20]
Supramolecular-enhanced dispersive liquid–liquid microextraction (SM-DLLME)	0.3	[21]
Microprecipitation technique	0.25	This study

Table 5. Application of the proposed procedure for determination of the cadmium contents of food samples (N=5).

Samples	**Concentration (μg g^{-1})**
Black pepper	1.05±0.08
Thyme	1.88±0.09
Hemp	0.55±0.06
Black cumin	3.28±0.04
Chili powder	1.63±0.04
Cuminum cyminum	0.68±0.04
Cinnamomum verum	1.15±0.09
Alpinia officinarum	2.18±0.08

Mean ± standard deviation

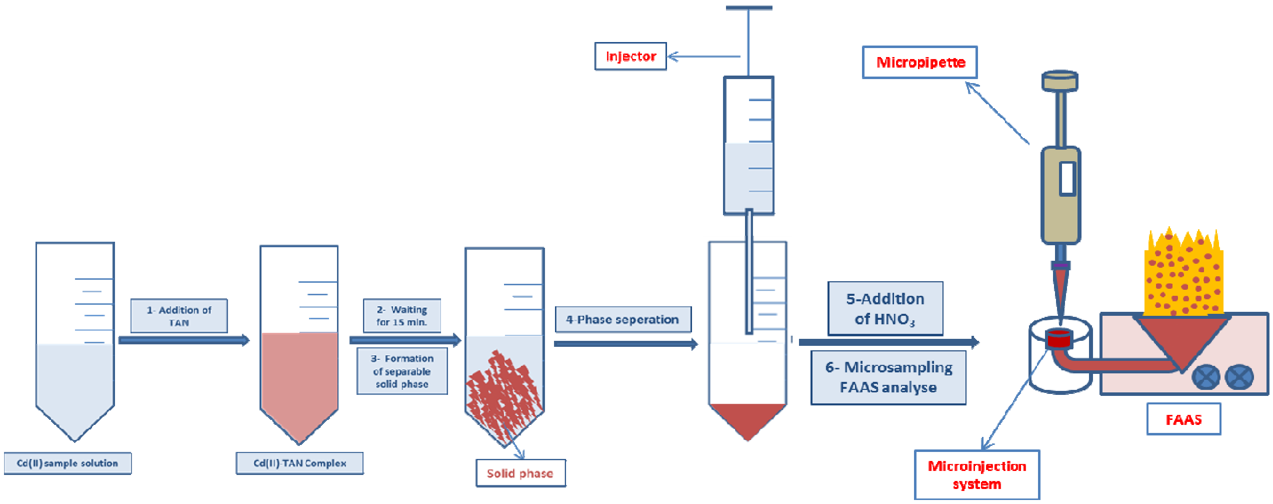
Injector
Micropipette
1- Addition of TAN
2- Waiting for 15 min.
3- Formation of separable solid phase
4-Phase seperation
5-Addition of HNO_3
6- Microsampling FAAS analyse
Cd(II)sample solution
Cd(II)-TAN Complex
Solid phase
Microinjection system
FAAS

Figure 1.

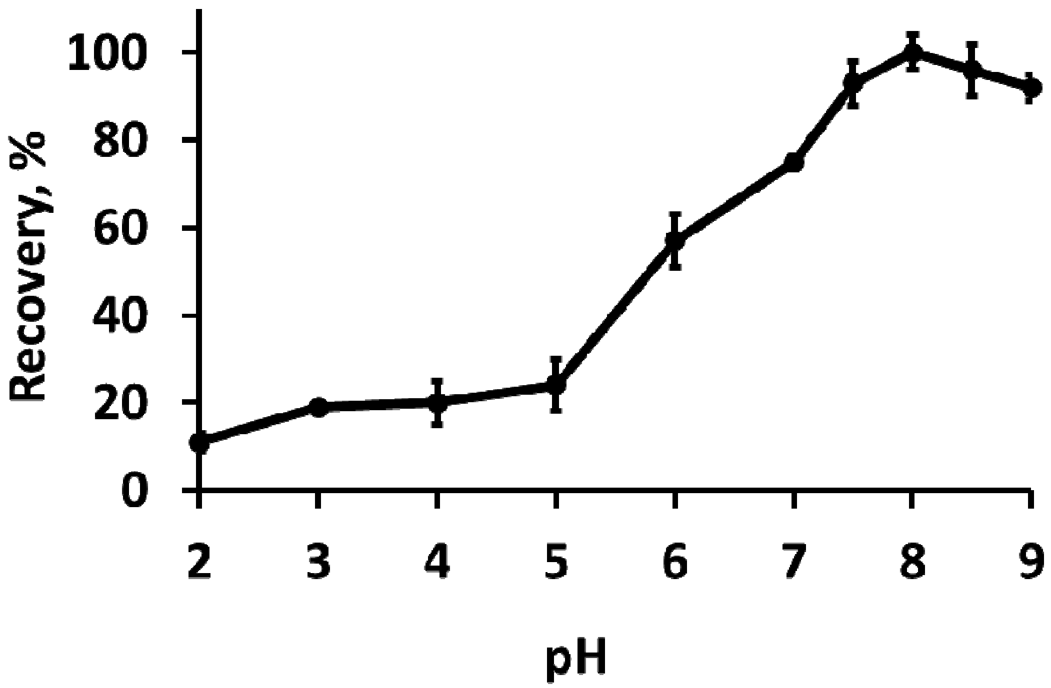

Figure 2

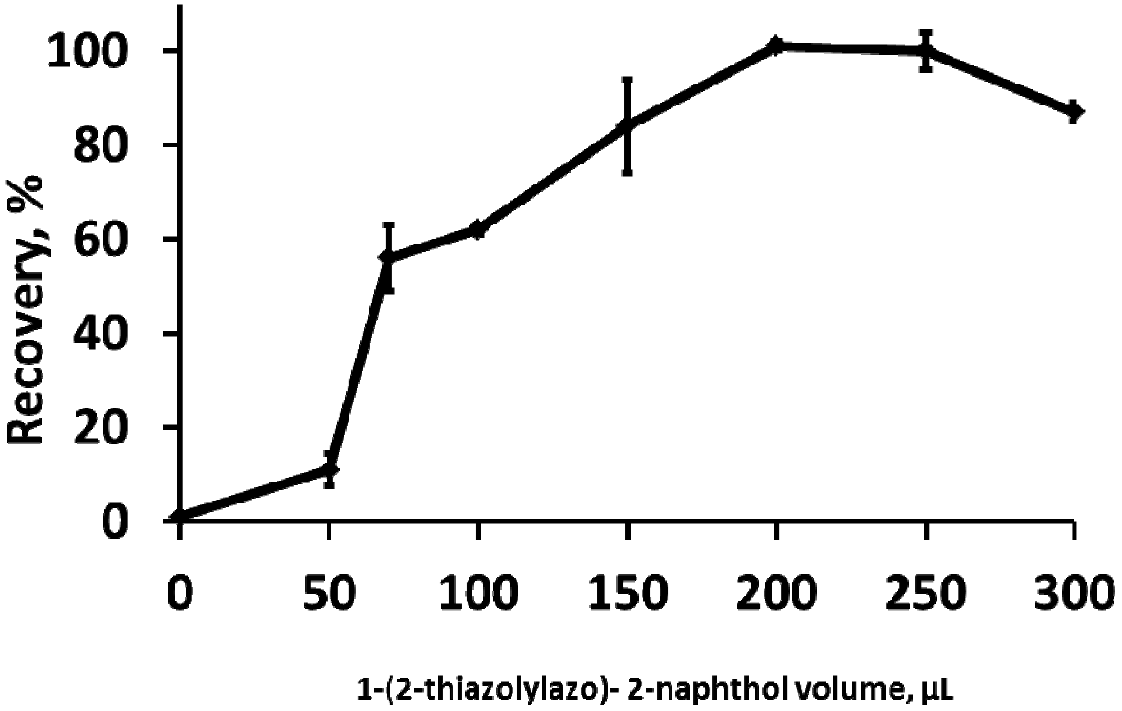
Recovery, %
100
80
60
40
20
0
0
50
100
150
200
250
300
1-(2-thiazolylazo)- 2-naphthol volume, µL

Figure 3

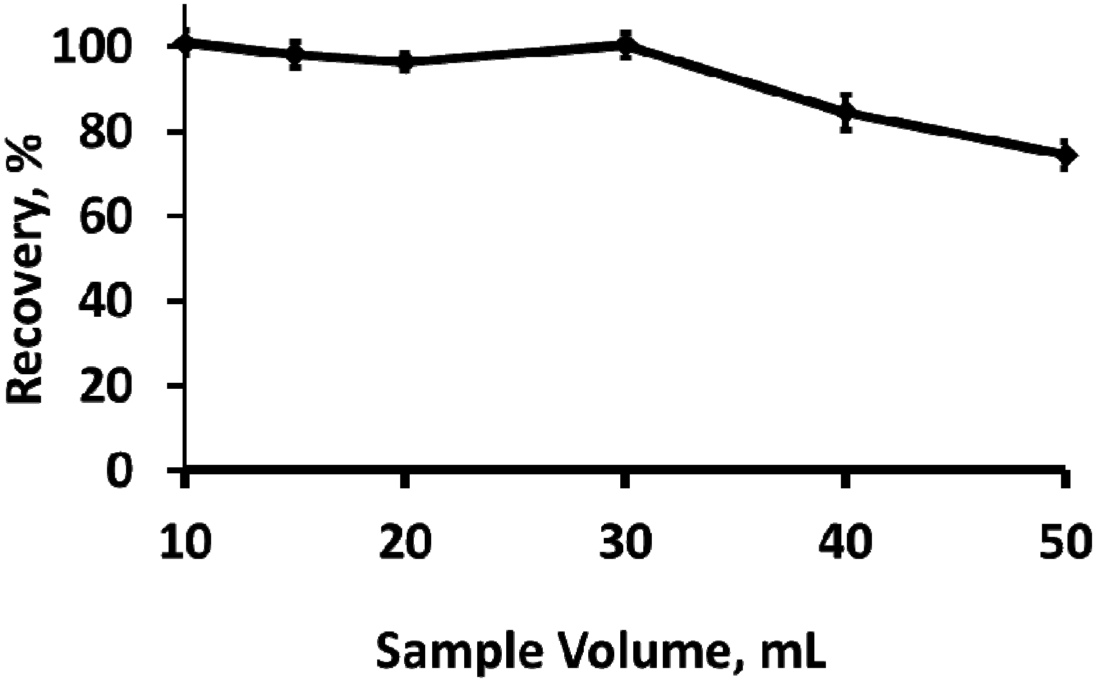

Figure 4

A green, novel and simple microprecipitation technique for separation and preconcentration of cadmium with 1-(2-thiazolylazo)-2-naphthol in food samples and determination by microsampling flame atomic absorption spectrometry

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