Vortex-assisted magnetic solid phase extraction of Pb and Cu in some herb samples on magnetic multiwalled carbon nanotubes

Dilek KAMAS1, Aslıhan KARATEPE1*, Mustafa SOYLAK2
1Department of Chemistry, Faculty of Arts and Science, Nevşehir Hacı Bektaş Veli University, Nevşehir, Turkey
2Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey

Abstract: This study is the development of a new solid phase extraction method based on using magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)2-naphthol (PAN) for separation, preconcentration, and flame atomic absorption spectrometric determination of Pb(II) and Cu(II). Optimization of the method was done by investigating pH effect, amount of magnetic multiwalled carbon nanotubes impregnated with PAN, eluent type and volume, matrix effects, and volume of the sample. The optimum adsorbent amount was found to be 75 mg and the optimum pH value was found as 5.5. The detection limits were 16.6 μg L\(^{-1}\) for Pb(II) and 18.9 μg L\(^{-1}\) for Cu(II). The relative standard deviations (RSD%) were less than 4%. Two certified reference materials: SPS-WW2 wastewater and NCS-DC73349 (bush branches and leaves) were used to test the validation of the method. The method was successfully applied to the analysis of Pb(II) and Cu(II) ions in daisy, mint, paprika, sage, rosemary, daphne leaves, heather, green tea, and Viburnum opulus samples.

Key words: Magnetic solid phase extraction, multiwalled carbon nanotubes, preconcentration, flame atomic absorption spectrometry, copper, lead

1. Introduction

In recent years, people tend to use some herbal teas as an alternative medicine to keep their health good or to heal the diseases, such as cancer, depression, liver diseases, colds, insomnia, and diabetes [1]. Herbal medicines are popular due to their perceived effectiveness in treating and preventing the disease, and it is believed that these treatments are natural and not harmful [2]. Daisy, mint, sage, rosemary, daphne leaves, heather, and green tea are commonly used for this purpose. Herbal teas can be defined as the herbal mixture made from their leaves, seeds, and/or roots of various plants [3].

Depending on the soil where these plants are grown and the water source used for irrigation, the plants can contain undesirable and/or undeclared substances as radioactive particles, pesticide residues, polycyclic aromatic hydrocarbons (PAHs), fumigants, and microbes including pathogens, mycotoxins, and heavy metals. These contaminants can be accumulated in herbs in different stages such as cultivation, storage, and their processing may cause adverse effects on the health of the consumers [4-6]. Thus, the analyses of such plants and spices is of great importance due to the risk of intake of hazardous materials because of overconsumption. Heavy metal contamination in herbs and the determination of its level is a great concern for chemists. Metals such as Al, Co, Cr, Cu, Fe, Mn, Ni, and Zn are essential plant nutrients; however, they may become toxic at higher concentrations [7]. Some activities also increase the concentrations of heavy metals in the environment such as, mining, metal ore smelting, industrial activities, and using pesticides and fertilizers in agriculture. Plants can accumulate heavy metals from the soil where they are planted as well as from the water source used for their irrigation or surrounding air. When the plants are grown in the contaminated soil without knowing whether they were contaminated or not, toxic heavy metals can enter into the food chain of human by accumulating in the plant [8,9]. European Commission considers mercury, nickel, lead, arsenic, and cadmium as major contaminants for the environment [10].

There are various papers reporting the works for the metal analysis in the herbs and spices by using different methods. These methods are: flame or electrothermal atomic absorption spectrometry, atomic fluorescence spectrometry, voltammetry, and inductively coupled plasma optical emission spectrometry [11,12]. The determination of trace elements...
such as aluminum, arsenic, cadmium, antimony, lead, iron, barium, zinc, manganese, copper, nickel, chromium, mercury and vanadium in various plant leaves and flowers, their teas, tinctures, and herbal medicine was carried out by different researchers [13-19]. When the concentrations of the metal ions in the sample are lower than the detection limit of the method, using a preconcentration method before determination becomes very important. Carbon nanotubes (CNTs) are used as novel solid phase extractors for various inorganic and organic materials at low concentrations. The structure of the CNTs can be defined as graphite sheet, which is rolled into a tube. They have different types such as multiwalled (MWNTs), single-walled (SWCNTs), or double-walled (DWCNTs) carbon nanotubes due to the number of carbon atom sheets in the nanotubes’ wall. Because of their extremely high surface/volume ratio, they are suitable adsorbents for many organic and inorganic materials in the preconcentration and separation studies, and they have been used for the purpose of metal ions’ preconcentration in many works [20-24]. Due to the rapid and effective technology, magnetic materials are attractive adsorbents for many scientists for separation, and their usage in solid phase extraction is a novel subject.

Using magnetic carbon nanotubes (M-CNTs) as magnetic solid phase provides sample pretreatment procedures, which are optimum and selective with some advantages such as shorter preparation time, minimized matrix effects, and less sample-preparation steps. Carbon nanotubes were used to remove, adsorb, or preconcentrate different environmental pollutants after modification with different magnetic materials. When it is compared with the other solid phase extraction methods, in magnetic solid phase extraction methods, sample pretreatment is very simple because there is no need to package the column with the adsorbent. Moreover, in case of batch mode operation, the phase can be separated quickly and easily by applying an external magnetic field [25-30].

In this work, nano-sized M-MWCNTs were prepared, and then impregnated with PAN, and used for the SPE of Pb(II) and Cu(II) in commonly consumed herbs such as daisy, mint, sage, daphne leaves, Viburnum opulus, rosemary, heather, green tea and paprika, which are used as tea and spice in Turkey. The determinations were made by using a flame AAS.

2. Experimental

2.1. Instrumentation

The pH values of all solutions were measured by using a digital pH meter (Sartorius PT-10). The solutions were mixed by a vortex mixer (VWR int., Germany). A Sonorex ultrasonic bath was used in the magnetic carbon nanotubes synthesis stage. The determinations of Pb(II) and Cu(II) ions were performed by flame atomic absorption spectrometer (Perkin-Elmer Inc., Waltham, MA USA, Analyst 300).

2.2. Chemicals and reagents

Unless specified, in all experimental studies analytical grade reagents and purified water (with a Milli-Q system, Millipore, USA) were used. M-MWCNTs and 1-(2-pyridylazo)-2-naphthol (PAN) were supplied form Sigma-Aldrich (St. Louis MO, USA). Nitric acid and acetone were purchased from Merck (Darmstadt, Germany). For the pH adjustments, phosphate buffers were used in the pH range of 4.0-7.0 and ammonium/ammonia buffer solutions were used for the pH range of 8.0-9.0.

2.3. Preparation of the magnetic M-MWCNTs impregnated with PAN

Nano-sized magnetic carbon nanotubes were prepared by using analytical grade FeCl₃·4H₂O, FeCl₃·6H₂O and ammonia (d: 0.903 g/cm³, 25%) solution. Coprecipitation method is used due to its easiness and high-volume capacity. This method is based on the coprecipitation of the dissolved Fe²⁺ and Fe³⁺ ions in aqua media by adding a base solution. According to this reaction, an initial concentration ratio of Fe³⁺: Fe²⁺ was 2 : 1 made by dissolving 0.3825 gram of FeCl₃·6H₂O and 0.7425 gram FeCl₃·4H₂O in a solution having a volume of 40 mL. After adding 0.25 g of MWNT to this solution, the mixture was heated on a magnetic stirrer under the argon atmosphere at 75 °C for 20 min. Then, 10 mL of NH₃ was added as drops while the solution was being stirred continuously. This procedure took approximately an hour, then the formation of the magnetic M-MWCNTs was seen by the black precipitate. The gained magnetic property of the product was checked by applying an external magnetic field. When it is compared with the other solid phase extraction methods, sample pretreatment is very simple because there is no need to package the column with the adsorbent. Moreover, in case of batch mode operation, the phase can be separated quickly and easily by applying an external magnetic field [25-30].

In this work, nano-sized M-MWCNTs were prepared, and then impregnated with PAN, and used for the SPE of Pb(II) and Cu(II) in commonly consumed herbs such as daisy, mint, sage, daphne leaves, Viburnum opulus, rosemary, heather, green tea and paprika, which are used as tea and spice in Turkey. The determinations were made by using a flame AAS.

2.4. Vortex-assisted magnetic solid phase extraction method (VA-MSPE) for preconcentration

A magnetic solid phase extraction method assisted by vortex was carried out by adding 10 µg Pb(II), 3 µg Cu(II) in a working solution (10 mL) that contains 75 mg of magnetic MCNT impregnated with PAN and 2 mL of pH 5.5 phosphate buffer solution. The solution was mixed for 2 min by a vortex, then, a strong neodymium permanent magnet was used for the separation of the adsorbent, which has gained magnetic property and the supernatants were separated by decantation. 3 mL HNO₃ in 10% acetone solution was used for elution by adding it to the adsorbent. Then, the mixture was mixed for
1 min on vortex to desorb the analytes. After isolating the extract from the adsorbent with the neodymium magnet, the absorbances were measured by a flame AAS. The schematic diagram of the M-MWCTs solid phase extraction procedure is depicted in Figure 1.

2.5. Sample preparation

The developed preconcentration method was applied to the determination of Pb(II) and Cu(II) in various herb samples, and the method is also applied to certificated SPS-WW2 wastewater and NCS-DC 73349 (bush branches and leaves). A total of 1.0 g of the herb samples and standard reference material were weighed and evaporated to dryness at approximately 100 °C by adding 10 mL HNO$_3$. Then, 10 mL of HNO$_3$ and 5 mL of H$_2$O$_2$ were added to the residual, and it was again evaporated to dryness at approximately 100 °C on a hotplate. The samples were filtered through a blue band filter paper, then diluted to a volume of 25 mL with distilled water, and the developed solid phase extraction method was applied successfully to determine Pb(II) and Cu(II) in herbs and spices such as daisy, mint, sage, daphne leaves, *Viburnum opulus*, rosemary, heather, green tea, and paprika.

3. Results

3.1. Effects of the pH value

Since the pH value affects the complexation of the metal ions, it was the first parameter to be optimized. Thus, pH value of the model solutions containing Pb(II) and Cu(II) ions was set to the desired values in the pH range of 2-10 by using buffer solutions. The results in which the optimum recovery was found as 5.5 is given in Figure 2. At high solution pH value, metal ions bind to OH$^-$ groups in the solution and cause precipitation. The pH value of 5.5 was applied for magnetic solid phase extraction of Pb(II) and Cu(II) on the magnetic M-MWCNTs in further studies.

3.2. Effect of the adsorbent amount

The adsorbent amount in the SPE methods is a significant parameter for the adsorption of the analytes. Therefore, the effects of the quantities of the magnetic M-MWCNTs impregnated with PAN varied from 25 to 100 mg were investigated on the recovery values of the analyte ions. According to the obtained results given in Figure 3, it was determined that Pb(II)
and Cu(II) were recovered quantitatively on adsorbent with adsorbent amount of 75-100 mg, and 75 mg of adsorbent was used for the following experiments.

3.3. Eluent type, concentration and volume effects
It is important to use an eluent, which effectively removes the adsorbed analytes in the adsorption studies. Thus, various organic and inorganic solvents at different concentrations have to be tested to choose the optimum eluent type. For this purpose, many desorbing solutions including 0.5-2 M HCl, 1-2 M HNO₃ and 1-3 M HNO₃ in 10% acetone were checked in the volume range of 1-5 mL. It is found that 3 mL 3 M HNO₃ in 10% acetone is the most appropriate solution for the desorption of the analytes from the adsorbent.

3.4. Effect of sample volume
To investigate the sample breakthrough volume, a number of experiments were performed to optimize the sample volume in the range of 10-50 mL while keeping the other conditions as optimum. It can be concluded from the results shown in Figure 4 that the presented SPE method can be performed quantitatively up to 30 mL of a sample volume.

3.5. Effect of vortex time
To investigate the effect of vortex time on the efficiency of the adsorption process for the analyte ions, 0.5-2.0 min was worked, and the optimum vortex time was chosen as 1 min for further studies.
3.6. Matrix effect
The effects of some possible matrix ions in real samples, such as alkaline and earth alkaline metal ions, some anions on the recovery of Pb(II) and Cu(II) ions were examined by addition of various concentration of possible matrix ions to the model solutions keeping the other optimum conditions same as found before. The experimental results shown in Table 1 indicates that this magnetic solid phase extraction method can be used to determine Pb(II) and Cu(II) accurately in the different type of real samples without matrix effects.

3.7. Analytical performance
Some analytical characteristics of the proposed method including preconcentration factor, limit of detection, and limit of quantification were listed in Table 2. The influence of sample volume on the solid phase extraction of analyte elements was investigated in the volume range of 10.0-50.0 mL. The extraction efficiencies of both of analytes were quantitative up to 30.0 mL of sample volume. The preconcentration factor was 10, when final volume is 3 mL. The inter-day and intra-day precision values of both analytes were below 4.0%.

The limit of detection (LOD = 3 × Sb/m) Here, 3×Sb: Three times of the standard deviation of 10 runs measurements of blank solutions and m: the slope of the calibration curve) was found as 16.6 µg L\(^{-1}\) and 18.9 µg L\(^{-1}\), and the limit of

![Figure 4. Effect of sample volume on the recovery of Pb(II) and Cu(II).](image)

| Ion      | Added as         | Concentration (mg L\(^{-1}\)) | Recovery, % |
|----------|------------------|-------------------------------|-------------|
|          |                  |                               | Pb          | Cu          |
| Na\(^+\) | NaNO\(_3\)       | 750                           | 93±2        | 87±3        |
| K\(^+\)  | KCl              | 750                           | 91±2        | 93±2        |
| Mg\(^2+\)| Mg(NO\(_3\))\(_2\).6H\(_2\)O | 2500                         | 95±2        | 103±1       |
| Ca\(^2+\)| Ca(NO\(_3\))\(_2\).4H\(_2\)O | 750                           | 98±2        | 97±2        |
| Fe\(^3+\)| Fe(NO\(_3\))\(_3\).9H\(_2\)O | 1                             | 91±2        | 95±2        |
| Zn\(^2+\)| Zn(NO\(_3\))\(_2\).6H\(_2\)O | 10                            | 97±2        | 93±1        |
| Mn\(^2+\)| Mn(NO\(_3\))\(_2\).4H\(_2\)O | 1                             | 88±4        | 90±4        |
| Co\(^2+\)| Co(NO\(_3\))\(_2\).6H\(_2\)O | 1                             | 91±2        | 92±2        |
| SO\(_4\)\(^2-\)| Na\(_2\)SO\(_4\) | 1250                          | 98±3        | 102±1       |
| Cl\(^-\) | KCl              | 750                           | 91±2        | 93±2        |
quantification (LOQ = 10 × Sb/m Here, 10 x Sb: Ten times of the standard deviation of the blank solutions (n = 10), and m: the slope of the calibration curve) was found as 55.4 µg L−1 and 62.9 µg L−1 for Pb(II) and Cu(II), respectively.

3.8. Cu and Pb in real samples

The developed preconcentration method was applied to the determination of Pb(II) and Cu(II) in various herb samples, and the method is also applied to certificated SPS-WW2 wastewater and NCS-DC 73349 (bush branches and leaves) samples. The results are given in Table 3. The method was also applied successfully to determine Pb(II) and Cu(II) in herbs and spices such as daisy, mint, sage, daphne leaves, Viburnum opulus, rosemary, heather, green tea, and paprika. The results were shown in Table 4. According to the results, only the green tea sample contains Pb with a concentration of 1.6 µg g⁻¹ while the others have concentrations below the detection limit. The maximum level for lead in fresh herbs and leaf vegetables is 0.1 (mg kg⁻¹ wet weight) according to Commission Regulations No 1881/2006 and No 629/2008. On the other hand, according to WHO, maximum permissible limit of copper is 0.1 mg L⁻¹, and the Cu concentrations in the samples were found in the range of 1.9-11.7 µg g⁻¹. The highest value was found for green tea sample.

### Table 2. Some analytical characteristics of the method.

| Parameters                  | Analytical feature of Pb | Analytical feature of Cu |
|-----------------------------|--------------------------|--------------------------|
| Regression equation, C (µg L⁻¹) | A = 0.008C-0.0009          | A=0.037C+0.0008          |
| Correlation coefficient (r) | 0.999                    | 0.999                    |
| LOD (3S_b/m) µg kg⁻¹       | 16.6                     | 18.9                     |
| LOQ µg kg⁻¹                | 55.4                     | 62.9                     |
| Preconcentration factor     | 10                       | 10                       |

### Table 3. Certified material analysis results (n = 3).

| Analyte          | SPS-WW2 waste water, µg L⁻¹ | NCS-DC73349 Bush Branches and Leaves, µg g⁻¹ |
|------------------|-----------------------------|---------------------------------------------|
|                  | Certificated value | Found           | Recovery % | Certificated value | Found           | Recovery % |
| Pb               | 500±3           | 530±2⁺          | 106        | 47±2           | 46.6±2.3        | 99         |
| Cu               | 2000±10         | 2210±1          | 110        | 6.6±0.08       | 6.8±0.7         | 103        |

⁺ mean ± standard deviation

### Table 4. Pb(II) and Cu(II) contents of real samples (n = 4).

| Sample                 | Concentration (µg g⁻¹) |
|------------------------|------------------------|
|                        | Pb | Cu |
| Daisy                  | BDL | 10.5±3.6⁺ |
| Mint                   | BDL | 10.3±1.3   |
| Viburnum opulus        | BDL | 4.7±0.3    |
| Paprika                | BDL | 5.1±0.7    |
| Sage                   | BDL | 4.1±0.7    |
| Daphne leaves          | BDL | 4.5±1.8    |
| Rosemary               | BDL | 3.9±1.1    |
| Heather                | BDL | 1.9±0.5    |
| Green tea              | 1.6±0.0 | 11.7±1.7  |

⁺ BDL: Below Detection Limit

⁺ mean ± standard deviation
3.9. Comparison to other extraction procedures in literature

The presented procedure was compared with some other preconcentration procedures in literature [29,31-38]. The comparison is given in Table 5. The presented procedure shows generally and comparatively low detection limit for analyte elements with some exceptions.

| Extraction method | Sample | LOD, μg L⁻¹ | PF  | Ref  |
|-------------------|--------|-------------|-----|------|
| Magnetic solid phase extraction | Water | Pb: 1.76 | 15  | [29] |
| Magnetic solid phase extraction | Water, food | Pb: 2.3 | 37-40 | [31] |
| Cloud point extraction | Water, food | Pb: 3.42 | 25  | [32] |
| Ionic liquid dispersive magnetic micro extraction | Water, plant, hair | Pb: 0.57 | 160 | [33] |
| Solid phase extraction | Water, cereal | Cu: 1.5 | 13  | [34] |
| Solid phase extraction | Water, herb, fish | Pb: 170 | 250 | [35] |
| MWCNTs- D2EHPA | Water, wastewater | Cu: 50 | 25  | [36] |
| Coprecipitation | Vegetable | Cu: 18 Pb: 35.9 | 50  | [37] |
| Vortex-assisted micro solid phase extraction | Water | Pb: 42 Cu: 22 | 35  | [38] |
| Magnetic solid phase extraction | Herb | Pb: 16.6 Cu: 18.9 | 10  | This work |

4. Conclusion

This work demonstrated a new environmentally friendly, simple, rapid, and low-cost method for the separation and detection of trace amounts of Pb(II) and Cu(II) in various samples when compared with the other solid phase extraction methods. In this method, new M-MCNTs was successfully synthesized and used as a favorable absorbent for VA-MSPE prior to FAAS determinations. By using this, SPE method Pb and Cu contents of daisy, mint, sage, daphne leaves, *Viburnum opulus*, rosemary, heather, green tea, and paprika samples were determined without interfering effects. One of the other advantages of the method was the removal of the adsorbent easily from the solution by only using a magnet in a very short time. Due to its advantages, this method can be successfully applied to water, food, and environmental samples containing complex matrix.

References

1. Ernst E. The efficiency of herbal medicine—an overview. Fundamental and Clinical Pharmacology 2005; 19: 405-409.
2. Stickel F, Patsenker E, Schuppan D. Review, herbal hepatotoxicity. Journal of Hepatology 2005; 43: 901-910.
3. Ravikumar C. Review on herbal teas. Journal of Pharmaceutical Sciences and Research 2014; 6(5): 236-238.
4. Bent S, Ko R. Commonly used herbal medicines in the United States: a review. The American Journal of Medicine 2004; 116 (7): 478-485.
5. Tripathy V, Saha A, Patel DJ, Basak BB, Shah PG, Kumar J. Validation of a QuEChERS-based gas chromatographic method for analysis of pesticide residues in Cassia angustifolia (senna). Journal of Environmental Science and Health, Part B 2016; 51: 508-518.
6. Tripathy V, Basak BB, Varghese TS, Ajoy S. Residues and contaminants in medicinal herbs- A review. Phytochemistry Letters 2015; 14: 67-78.
7. Filipiak-Szok A, Kurzawa M, Szyk E. Determination of toxic metals by ICP-MS in Asiatic and European medicinal plants and dietary supplements. Journal of Trace Elements in Medicine and Biology 2015; 30: 54-58.
8. Ghaderian, M, Ravandi AAG. Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. Journal of Geochemical Exploration 2012; 123: 25-32.
9. Gupta S, Pandotra P, Gupta AP, Sharma JKG, Ram G et al. Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of Zingiber officinale collected from different locations of North Western Himalayas by atomic absorption spectroscopy. Food and Chemical Toxicology 2010; 48: 2966-2971.

10. European Commission. 2006. Commission Regulation (EC) No 1881/2006. Official Journal of the European Communities R1881:16-23.

11. Smichowski P, Londonio A. The role of analytical techniques in the determination of metals and metalloids in dietary supplements: A review. Microchemical Journal 2018; 136: 113-120.

12. Injiang U, Noyrod P, Siangproh W, Dungchai W, Motomizu et al. Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. Analytica Chimica Acta 2010; 668 (1): 54-60.

13. Gomez MR, Cerutti S, Sombra LL, Silva MF, Marti’nez LD. Determination of heavy metals for the quality control in Argentinian herbal medicines by ETAAS and ICP-OES. Food and Chemical Toxicology 2007; 45: 1060-1064.

14. Arpadjan S, Celik G, Taskesen S, Gucer S. Arsenic, cadmium and lead in medicinal herbs and their fractionation. Food and Chemical Toxicology 2008; 46: 2871-2875.

15. Caldas ED, Machado LL. Cadmium, mercury, and lead in medicinal herbs in Brazil. Food and Chemical Toxicology 2004; 42: 599-603.

16. Thongsaw A, Chaiyasith WC, Sananmuang R, Ross GM, Ampiah-Bonney RJ. Determination of cadmium in herbs by SFODME with ETAAS detection. Food Chemistry 2017; 219: 453-458.

17. Pytlakowska K, Kita A, Janoska P, Połowniak M, Kozik V. Multi-element analysis of mineral and trace elements in medicinal herbs and their infusions. Food Chemistry 2012; 135: 494-501.

18. Nookabkaew S, Rangkadilok N, Satayavivad J. Determination of trace elements in herbal tea products and their infusions consumed in Thailand. Journal of Agricultural and Food Chemistry 2006; 54(18): 6939-6944.

19. Divrikli U, Horzum N, Soyak M, Elci L. Trace heavy metal contents of some spices and herbal plants from western Anatolia-Turkey. International Journal of Food Science and Technology 2006; 41: 712-716.

20. Tuzen, M, Saygi KO, Soyak M. Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes. Journal of Hazardous Materials 2008; 152: 632-639.

21. Kosa SA, Al-Zhrani G, Salam MA. Removal of heavy metals from aqueous solutions by multi-walled carbon nanotubes modified with 8-hydroxyquinoline. Chemical Engineering Journal 2012; 181-182: 159-168.

22. Wadhwa SK, Tuzen M, Kazi TG, Soyak M. Graphite furnace atomic absorption spectrometric detection of vanadium in water and food samples after solid phase extraction on multi walled carbon nanotubes. Talanta 2013; 116: 205-209.

23. Shamspur T, Mostafavi A. Application of modified multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration trace amounts of Au(III) and Mn(II). Journal of Hazardous Materials 2009; 168: 1548-1553.

24. Herrero-Latorre, C, Barciela-García J, García-Martín S, Pena-Creciente RM, Otarola-Jimenez J. Magnetic solid-phase extraction using carbon nanotubes as sorbents: A review. Analytica Chimica Acta 2015; 892: 10-26.

25. Salam MA, El-Shishawy RM, Obaid AY. Synthesis of magnetic multi-walled carbon nanotubes/magnetite/ chitin magnetic nanocomposite for the removal of Rose Bengal from real and model solution. Journal of Industrial and Engineering. Chemistry 2014; 20: 3559-3567.

26. Soyak M, Erbas, Z. Vortex-assisted magnetic solid phase extraction of Cd(II), Cu(II) and Pb(II) on the Nitroso–R salt impregnated magnetic Amberisorb 563 for their separation, preconcentration and determination by FAAS. International Journal of Environmental Analytical Chemistry 2018; 98:799-810.

27. Ailar-Arteaga K, Rodriguez JA, Barrado E. Magnetic solids in analytical chemistry: A review. Analytica Chimica Acta 2010; 674: 157-165.

28. Wang Y, Xie J, Wu Y, Hu X, Yang C et al. Determination of trace amounts of Se(IV) by hydride generation atomic fluorescence spectrometry after solid-phase extraction using magnetic multi-walled carbon nanotubes. Talanta 2013; 112: 123-128.

29. Khan M, Yilmaz E, Soyak M. Vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II)on silica coated magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)-2-naphthol. Journal of Molecular Liquids 2016; 224: 639-647.

30. Yilmaz I, Soyak, M. Preparation and characterization of magnetic carboxylated nanodiamonds for vortex-assisted magnetic solid-phase extraction of ziram in food and water samples. Talanta 2016; 158: 152-158.

31. Khan M, Yilmaz E, Sevinc B, Sahmetlioglu E, Shah J et al. Preparation and characterization of magnetic allylamine modified graphene oxide-poly(vinyl acetate-co-divinylbenzene) nanocomposite for vortex assisted magnetic solid phase extraction of some metal ions. Talanta 2016; 146: 130-137.

32. Citak D, Tuzen M. A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry. Food and Chemical Toxicology 2010; 48(5): 1399-1404.
33. Yilmaz E, Soylak M. Ionic liquid-linked dual magnetic microextraction of lead(II) from environmental samples prior to its micro-sampling flame atomic absorption spectrometric determination. Talanta 2013; 116: 882-886.

34. Divrikli U, Akdogan A, Soylak M, Elci L. Solid-phase extraction of Fe(III), Pb(II) and Cr(III) in environmental samples on amberlite XAD-7 and their determinations by flame atomic absorption spectrometry. Journal of Hazardous Materials 149; 2007: 331-337.

35. Pourjavid MR, Arabieh M, Sehat AA, Rezaee M, Hosseini MH et al. Flame atomic absorption spectrometric determination of Pb(II) and Cd(II) in natural samples after column graphene oxide-based solid phase extraction using 4-Acetamidothiophenol. Journal of the Brazilian Chemical Society 2014; 25(11): 2063-2072.

36. Vellaiichamy S, Palanivelu K. Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture. Journal of Hazardous Materials 2011; 185: 1131-1139.

37. Feist B, Mikula B, Pytlakowska K, Puzio B, Buhl F. Determination of heavy metals by ICP-OES and F-AAS after preconcentration with 2,2′-bipyridyl and erythrosine. Journal of Hazardous Materials 2008; 152: 1122-1129.

38. Baghban N, Yilmaz E, Soylak M. Nanodiamond/MoS2 nanorod composite as a novel sorbent for fast and effective vortex-assisted micro solid phase extraction of lead(II) and copper(II) for their flame atomic absorption spectrometric detection. Journal of Molecular Liquids 2017; 234: 260-267.