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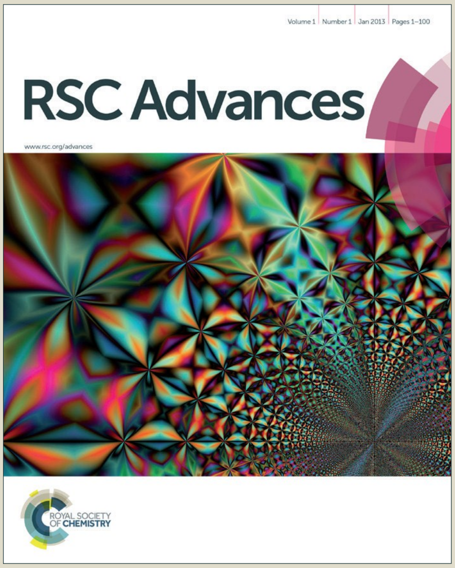

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Supramolecular solvent-based microextraction method for cobalt traces in food samples with optimization plackett-burman and central composite experimental design

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ABSTRACT

A new microextraction method based on formation of supramolecular solvent (Ss) was developed by using of chemometric optimization method for cobalt determination with microsampling flame atomic absorption spectrometry (MS-FAAS). 1-decanol/ THF was used to obtain supramolecular solvent, which ensure the formation of micelles in the nano and molecular size and to transfer the diethyldithiocarbamate (DDTC)-cobalt(II) complex from the aqueous phase to the extraction phase media. The optimization strategy was carried out by using of Plackett-Burman Design (PBD) and Central-Composite Design (CCD). Statistically significant parameters such as pH, the volume of ligand (DDTC), the volume of supramolecular solvent (1-decanol/THF) and centrifugation time were investigated by using of Plackett-Burman design. Central-composite design was used to determine optimal condition of these parameters. The optimum experimental conditions obtained were pH 6, 125 µL of 1-decanol, 450 µL of THF, 300 µL of DDTC (0.1 %, w/v) and 8 min of centrifugation time. The relative standard deviation (RSD), limit of detection (LOD), limit of quantitation (LOQ) and preconcentration factor (PF) were 1.51 % (n=8, 94-98 %), 1.89 µg L^{-1}, 6.32 µg L^{-1} and 30 respectively. The method were applied to the certified reference materials of TMDA 53.3 water, TMDA 64.2 water, SPS-WW2 waste water, Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Scallion (Salad Onion), (NCS

ZC73033) to validation. The microextraction method was also successfully applied to determine cobalt concentrations by microsampling FAAS in water, cereal, powdered beverage and fruit samples.

Keywords Supramolecular solvent microextraction, Food, Flame atomic absorption spectrometry, Plackett-Burman design, Central-Composite design.

1. Introduction

Cobalt metal ion has biological importance due to it is one of component of vitamin B_{12}. So, cobalt metal plays an important role in our life. However, the metal may also be harmful, if human are exposed to large amounts of cobalt. High levels of cobalt can result in lung and heart effects and dermatitis. The respiratory system of workers in cobalt industry due to cobalt metal mixed with tungsten carbide particles is the main target organ of cobalt, which are asthma, fibrosing alveolitis, and lung cancer. Other target organs include the nervous system, the thyroid gland, the hematopoietic system and the myocardium for cobalt toxicology .[1,2] Cobalt is a key element that has been used for environmental and toxicological monitoring.[3,4]

The determination of trace element species in various media has been performed by using of different sample preparation techniques.[5,6] Classical liquid–liquid extraction (LLE) and solid-phase extraction (SPE) methods in analytical applications often require large amounts of organic solvents, some of which are harmful and contaminate the environment due to their high vapor pressure. Therefore, a new trend in analytical chemistry is to develop new miniaturized methodologies. A number of miniaturized microextraction methods for trace metal ions[7,8] and organic compounds[9,10] have been developed to solve these problems. Ionic liquid-based dispersive microextraction (IL-DLLME),[11,12] solid-phase microextraction,[13] solidified floating organic drop microextraction (SFODME),[14] bar adsorptive microextraction (BAME),[15] cold-induced aggregation microextraction (CIAME),[16] dispersive liquid-liquid microextraction (DLLME),[17-20] supramolecular solvent-based microextraction (Ss-ME),[21,22] reverse micelle coacervate-based microextraction[23] etc. are widely used in recent years as a sample pretreatment technique.

Ss-ME has been applied to the determination of hydrophobic organic compounds,[24] metals[25] and anionic species[26] which are mainly from environmental and biological liquid samples. Supramolecular solvents (Ss) are nano-structured liquids which are generated from the amphiphiles. Supramolecular structures are water-immiscible liquids and are made up of aggregates such as micelles in the bulk aqueous phase. Large supramolecular aggregates dispersed in a continuous phase like water. The driving forces for the extraction are hydrophobic interactions, hydrogen bonding, e.g., between the hydrophobic metal complex and aggregates. Trace metal ions in the form of their hydrophobic metal complexes can be easily extracted into the surfactant rich phase from the aqueous solution.[27]

Generally two different strategies for optimization of analytical methods have been used as a screening way, which are one factor-at-a-time (OFAT) and chemometric methods such as response surface methodology (RSM) based on statistical design of experiments (DOE).[28, 29]

The traditional analytical methods used to determine organic compounds or metals from different samples based on usually one-factor-at-a-time (OFAT) approach. The effect of each parameter individually was studied while holding the other parameters at a specific value. The OFAT method has some drawbacks such as requiring long period of time, neglecting the effect of interactions with other species and screening a large amount of target analyte. The RSM based on statistical design of experiments (DOE) takes into account interactions between the studied variables and concludes more accurate combinations and also, provides optimum analytical data can be produced from the chemometric calculations.[28] Plackett-Burman design (PBD) and central composite design (CCD) under statistical design of experiments (DOE) methods are used in RSM for screening process [31].

The applications of chemometric methods are becoming widespread application, owing to the availability of designed statistical data in separation and preconcentration studies for metals at trace level. Instead of doing more experimental studies, the using of the optimal experimental design is effective for studying fewer experiments. These designs are useful in avoiding experiments performed under optimum conditions, for which unsatisfactory results might occur [32].

In order to use these advantages of Ss-ME techniques and chemometric optimization methods, this paper describes a Ss-ME procedure combined with microsampling flame atomic absorption spectrometry (MS-FAAS) for separation and preconcentration of trace level of cobalt in water, cereal, powdered beverage and fruit samples.

2. Experimental

2.1. Materials

Cobalt stock solution (1000 mg L^{-1}) was prepared by dissolving appropriate amounts of $Co(NO_3)_2.6H_2O$ in ultra-pure water and was diluted daily for obtaining reference and working solutions. A solution of % 0.1 (w/v) sodium-diethyldithiocarbamate (Sigma-Aldrich, US) solution used as chelating reagent to form metal complex with Co(II) was prepared with using ethanol.

The pH values were adjusted by addition of phosphate buffer solutions (0.1 mol L^{-1} $H_2PO_4^-$/ 0.1 mol L^{-1} H_3PO_4) for pH 2 and ammonium buffer solutions (0.1 mol L^{-1} NH_4^+/0.1 mol L^{-1} NH_3) for 6 and 8. 1-decanol/THF, 30 % (v/v) H_2O_2 and 65 % HNO_3 were used for digestion of cereal, powdered beverage and fruit samples. All glassware used were kept in HNO_3 (10 %) overnight and washed with tap water and then washed with ultra-pure water before using.

The validation of this procedure was checked by studying of TMDA 53.3 water (National Water Research Institute, Ontario, Canada), TMDA 64.2 water (National Water Research Institute, Ontario, Canada), SPS-WW2 waste water (Spectrapure Standards AS, Oslo, Norway), Oriental Basma Tobacco Leaves (INCT-OBTL-5) ((Institute of Nuclear Chemistry and Technology, Poland) and Scallion (Salad Onion), (NCS ZC73033) (LGC Standards, Teddington, Middlesex, UK), certified reference materials.

2.2. Instruments

Perkin-Elmer 3110 Flame atomic absorption spectrometer equipped with hollow cathode lamp was used for cobalt absorbance measurements. Air-acetylene was used as an atomizing medium; all measurements were carried out without background correction. All instrumental parameters were adjusted as recommended by the manufacturer. Micro-sampling introduction system was home-made material which was made from Teflon and connected to FAAS nebulizer.[23] Ultrasonic water bath (Sonorex) was used to form the formation of micelles and to transfer the diethyldithiocarbamate-cobalt(II) complex from the aqueous phase to the extraction phase. The separation of aqueous and organic phase was achieved via a centrifuge-Hettich Rotina 38 equipped with an angle rotor (8 x 50 mL, 5000 rpm). The pH values were determined with a model Nel pH 900 digital pH meter equipped with combined glass electrode. Ultra-pure water (18.2 MΩ cm) obtained from Millipore water purification device was used in all cases (standard solution preparation and dilutions).

2.3. Software

Minitab13.2 (Minitab Inc., State College, PA) statistical software program was used to process the experimental data of PBD and CCD. And also, STATISTICA software program was used to draw graphics.

The relationships of analytical parameters with each other were graphed to evaluate the results using the STATISTICA 7.0 statistical software package developed by Stat Soft.

2.4. Supramolecular Solvent-based Microextraction (Ss-ME) Procedure

Preconcentration studies for cobalt(II) were carried out using 10 mL of synthetic solutions. 10 mL of aqueous sample solution containing 100 µg L^{-1} Co (II) and 2.5 mL acetate buffer (pH: 6.0) was placed in a 50 mL conical centrifuge tube. Then, 0.3 mg sodium-diethyldithiocarbamate (Na-DDTC) solution prepared in ethanol was added as chelating reagent to form Co(II) metal complex into the sample solution. After the formation of $Co(DDTC)_2$ complex, 450 µL of tetrahydrofuran and 125 µL of 1-decanol was rapidly injected into the solution. A cloudy solution (supramolecular solvent, 1-Decanol/THF/H_2O) was formed by keeping of ultrasonic bath for 1 min. Then, this cloudy solution was centrifuged at 4000 rpm for 8 min and the fine droplets sediment at the upper of the conical test tube was obtained by centrifugation. The lower water phase was taken up with a pipette and discarded. A small droplet of extraction solution (about 150 µL) containing target analyte was completed to 500 µL with methanol. The 100 µL of this sedimented solution was taken with a micropipette and the analyzing of the cobalt was performed by micro-sampling introduction system connected to FAAS nebulizer. Continuous aspiration mode was used in all measurements.

2.5. Sample Preparation and Applications

The developed method was applied to the fortified water certified reference materials, which are TMDA 53.3 water, TMDA 64.2 water and SPS-WW2 waste water, Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Scallion (Salad Onion), (NCS ZC73033) for verifying the validity of the proposed method. The cereal samples (corn, heat, green lentil, barley and vetch) and the powdered beverage samples (lemon-flavored, cherry-flavored, rosehip-flavored powdered beverages) were acquired from supermarket in Kayseri, Turkey. The fruit samples (Vibirnum opulus-guelder rose, grape and plum) were collected from a town in Kayseri, Turkey.

Cereal and fruit samples were washed with tap water and then with ultra-pure water, several times to remove impurities. Then, samples were dried in a drying oven. The samples were separately ground in an agate mortar to obtain a homogeneous sample. 0.25 g homogenized cereal samples were accurately weighed in 100 mL of beakers. The samples were digested by using a mixture of concentrated HNO_3 (65 %, 10 mL) and H_2O_2 (30 %, 5 mL) on hot a plate at 100 °C. This solution was evaporated on the hot plate until to dryness. This procedure was repeated once more, till clear transparent solutions were obtained. Blank samples without analyte but with the same amount of acids were subjected to the same digestion procedure. After cooling, the residue was transferred to the 50 mL conical-bottom glass centrifuge tube by using ultra-pure water. The mixture was then filtrated cellulose nitrate membrane filter of 0.45 μm size and 47 mm diameter (Osmonics, Westborough, MA, USA). The sample pH was adjusted to diluted sodium hydroxide (0.01 mol L^{-1}) solution and 6.0 using buffer solution and then, developed Ss-ME procedure was applied.

3. Results and discussion

3.1 Optimization Strategy

It is necessary to optimize some important parameters that may affect the yield of cobalt recovery. So, optimization studies was started by selecting the low (-) and high (+) values of pH (P), the volume of ligand (L), the volume of 1-decanol (D), the volume of THF (T) and centrifugation time (C). Minimum and maximum ranges of the five variables were determined for optimization of the method (Table 1). Optimizations were performed in two steps by using of Plackett–Burman design (PBD) and Central Composite Design (CCD) multivariate techniques.

3.2. Plackett–Burman design (PBD)

PBD study with sixteen runs was developed to determine the influence of experimental variables on the microextraction efficiency of cobalt in the Ss-ME technique. The sample pH (P), the volume of 1-decanol (D), the volume of ligand (L), the volume of THF (T) and centrifugation time (C) were selected for optimization of the Ss-ME method. As can be seen from Table 2, the volume of 1-decanol (D), the volume of ligand (L) and the volume of THF (T) were the most important parameters. Table 2 showed that the maximum recovery of Co(II) was observed at lower (-) level of the 1-decanol, THF and ligand volumes, while the pH and centrifuge time were at high level (experiment 1 and 16). When the 1-decanol, THF and ligand volumes were at (+) level, the percent recovery for Co(II) was 74–83 % (experiment 4 and 5). So, 1-decanol, THF and ligand volumes had highly important effects on recovery of Co(II) and the higher (+) level of these parameter had negative effects on the % recovery of Co(II). But, the pH and centrifuge time had no significant effects on the formation and extraction of $Co(DDTC)_2$ complex. Pareto Chart (Fig. 1) was used in order to identify the interactions and significant effects on the % recovery of Co(II) (p = 0.05). The resulted data of the developed method were evaluated by analysis of PBD and visualized by using standardized (p~ 95.0 % confidence interval) effects in Pareto chart.

3.3 Central composite design (CCD)

After screening the variables that had not any effect, the remaining four factors that had significant effect on the Co(II) recovery were optimized to provide the maximum recovery by applying the central composite design (CCD). The sample pH, the volume of 1-decanol (D), the volume of ligand (L), and the volume of THF (T) were evaluated as the most important parameters. The CCD design had twenty four different experiment designs with three central points were obtained. Variables and recoveries were shown for each different design in Table 3. It was observed that at low level of D (-), the recoveries of Co (II) were not at maximum value (experiments

2, 3, 6, 7, 10, 11, 14 and 15, Table 3). The maximum recovery values were obtained at (+) level of D (experiments 1, 4, 8, 12, 16, 18, 20, 22 and 24). The recoveries of Co(II) were not high at low levels of D and T (-) (experiments 2 and 3). The results indicated that the minimum volumes of D and T were not enough for the extraction of $Co(DDTC)_2$ complex. Maximum recoveries of Co(II) were obtained at high volumes of D (1-decanol) and T (THF). The maximum recoveries for Co(II) were obtained at average levels of pH, 1-decanol volume and THF volume (experiment 22) and all four variables ($_aP^2$, $_bD^2$, $_cL^2$ and $_dT^2$) (experiment 1).

The study of estimated three dimension surfaces response for variables ([D–L], [T–D] and [pH–D] was estimated by quadratic equation, indicated that the maximum recovery of Co(II) was observed 6 for pH, 300 µL for ligand volume, 125 µL for 1-decanol volume, 450 µL for THF volume as optimum values (Fig. 2a, b, c).

3.4. Influence of Sample Volume

After the optimal values were determined utilizing PPD and CCD experimental designs, the effect of sample volumes were studied to investigate the recovery of cobalt in different sample volumes ranging from 10 to 40 mL to obtain high preconcentration factor. [33-39] The results were shown in Fig. 3. It was found that the maximum recoveries could be obtained up to 15 mL. But, the recoveries decreased with increasing sample volume. Thus, sample volume of 15 mL was selected as a suitable sample volume. The maximum recovery % was found to be with starting sample volume up to 15 and the preconcentration factor (PF) was calculated as 30 considering the last volume is 500 µL.

3.5. Influence of Coexisting Ions

Due to the interference effect of coexisting ions, [40-47] determinations of metals at trace levels by instrumental methods are very difficult. Because, the interferences compete with other ions for chelating with ligand and give rise to the co-extraction (solvent extraction of two or more compounds, simultaneously) with Co(II). In order to determine the effect of some common coexisting ion interferences, model solutions were prepared that contain 0.1 µg mL^{-1} Co(II) and different amount of interference ions (alkali, alkaline earth and other ion and metal ions) and the procedure given in Section 2.4 was applied to these solutions. The tolerance limits of the coexisting ions that found experimentally were given in Table 4. As can be seen, the interferences had no obvious influence on the determination of the cobalt recovery % up to the maximum amount.

3.6. Method validation

The analytical performance of the Ss-ME method was investigated in determining of Co(II), under the optimal conditions obtained by using of the statistical design of experiments (DOE) method. A calibration curve was obtained by preconcentration series of cobalt solutions added in increasing concentrations according to the developed microextraction method. The linear dynamic range (LDR) was obtained between 1 and 10 µg mL^{-1} for cobalt and the correlation coefficient (R^2) was found as 0.998. Calibration curve equation was A= 0.0019 + 0.047C, where A is the absorbance (peak area) and C is cobalt concentration in µg mL^{-1}. The relative standard deviation (RSD) was found 1.51 % for eight replicate cobalt measurements (94-98 %). The limit of detection defined as CL =$3S_B$/m (where CL, S_B, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 1.89 µg L^{-1}. [48] The limit of quantification (LOQ) value was 6.32 µg L^{-1}.

Under the optimized conditions, addition-recovery test was applied to the determination of cobalt metal of cereal and powdered beverage samples. As shown in Table 5, the recoveries of cobalt ranged from 93 % to 100 % and obtained final values that determined by the presented microextraction method-microsampling FAAS were in a good agreement with the added values.

The method was also evaluated by performing certified reference materials (CRMs) which were TMDA-53.3 water, TMDA-64.2 water SPS-WW2 waste water, Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Scallion (Salad Onion), (NCS ZC73033) and assessed whether the results of cobalt were compatible with the certified reference material contents. Table 6 shows the results from the analysis of CRMs in optimum condition. It can be said that the results obtained are in a good agreement in terms of cobalt contents with the CRMs. That is, the results shown Table 6 confirm the validity of the proposed method.

3.7. Application to real samples

The proposed Ss-ME procedure was successfully applied to the determination of cobalt contents of cereal, fruit and powdered beverage samples obtained from Kayseri, Turkey. The cobalt concentrations in samples were given Table 7.

3.8. Comparison with Other Microextraction Methods

A comparison of the represented method with other approaches reported in the literature for determination of cobalt in different real samples by microextraction procedure is given in Table 8. In comparison with other preconcentration methods, RSD, PF/EF and LOD obtained by the Ss-ME method are comparable to or better than other reported microextraction methods. The supramolecular microextraction combined with microsampling flame atomic absorption spectrometry has been previously developed and reported for the determination of Co(II) in water samples via OFAT and with Co(II)-N-Benzoyl-N,N-diisobutylthiourea chelates. [51] The analytical figures of presented work is better than our OFAT study for cobalt(II) (Table 8). Chemometric optimization procedure for presented work has some advantages including time saving procedure and neglecting the effect of interactions with other species to OFAT procedure.Therefore, the Ss-ME method with chemometric optimization that is developed with microsampling-FAAS can be used for the determination of cobalt in water, cereal fruit and powdered beverage samples.

4. Conclusions

The presented method offers a new combination of Ss--ME method with chemometric optimization for the preconcentration of cobalt in water, cereal, fruit and powdered beverage samples by microsampling FAAS. PBD and CCD designs provide fast and efficient experiments and also less consumption of organic solvents that are used during the optimization of variables. Instead of using more toxic organic solvents that damage the environment, we also used supramolecular solvent referred as a "green solvent" as extraction solvent in the microextraction study. The proposed method is a green method because very small amounts of organic solvents (1-decanol: 125 µL, THF: 450 µL) are used. Target analytes can be analyzed with microsampling FAAS in very small final sample volume (100-150 µL). This microextraction procedure is a quite easy, rapid and low-cost technique. Furthermore, this procedure can also be easily applied in many laboratories for separation and preconcentration of cobalt in different real samples.

References

1 V. A. Lemos, R. S. Franca, B. O. Moreira, *Sep. Purif. Technol.*, 2007, **54**, 349–354.

2 D. Lison, *Handbook on the Toxicology of Metals, Volume II: Specific Metals.,* eds. G. F. Nordberg, B. A. Fowler, M. Nordberg, Elsevier, Amsterdam, 4th Edition, 2015, 34, 743–763.

3 M. Soylak, L. Elci, M. Dogan, *Anal. Lett.*, 1997, **30**, 623–631.

4 M. Soylak, L. Elci, I. Narin, M. Dogan, *Trace Elemen. Eletroly.*, 2001, **18**, 26–29.

5 B. N. Kumar, D.K.V. Ramana, Y. Harinath, K. Seshaiah, M.C. Wang, *J. Agr. Food. Chem,.* 2011, **59**, 11352-11358.

6 G. Z. Tsogas, D. L. Giokas, E. K. Paleologos, A. G. Vlessidis, N. P. Evmiridis, *Anal.Chim. Acta*, 2005, **537**, 239–248.

7 Z. Shi, H.K. Lee, *Anal. Chem.*, 2010, **82**, 1540–1545.

8 Q. Wu, Q. Chang, C. Wu, H. Rao, X. Zeng, C. Wang, et al., *J. Chromatogr. A*, 2010, **1217**, 1773–1778.

9 A.R. Fontana, M.M. de Toro, J.C. Altamirano, *J. Agr. Food. Chem,.*, 2011, **59**, 3559-3565.

10 E.A. Souza-Silva, J. Pawliszyn, *J. Agr. Food. Chem.,* 2015, **63**, 4464-4477.

11 M. Sun, J. Feng, H. Qiu, L. Fan, X. Li, C. Luo, *Talanta*, 2013, **114**, 60–65.

12 M. S. Bidabadi, S. Dadfarnia, A. M. H. Shabani, *J. Hazard Mater.*, 2009, **166**, 291–296.

13 C. Almeida, J.M.F. Nogueira, *J. Chromatogr.*, 2014, **1348A**, 17–26

14 D.B.G. Williams, M.J. George, L. Marjanovic, *J. Agr. Food. Chem.,* 2014, **62**, 7676-7681.

15 A.N. Anthemidis, K.G. Ioannou, *Talanta*, 2009, **79**, 86–91.

16 M. Soylak, E. Yılmaz, *Desalination*, 2011, **275**, 297-301.

17 J.V. Maciel, B.M. Soares, J.S. Mandlate, R.S. Picoloto, C.A. Bizzi, E.M.M. Flores, F.A. Duarte, *J. Agr. Food. Chem.,* 2014, **62**, 8340-8345.

18 R. Suarez, B. Horstkotte, C.M. Duarte, V. Cerda, *Anal. Chem.*, 2012, **84**, 9462–9469.

19 S. Jafarvand, F. Shemirani, *J. Sep. Sci*., 2011, **34**, 455–461.

20 S. Jafarvand, F. Shemirani, *Anal. Methods***,** 2011, **3**, 1552-1559.

21 Amjadi M, Manzoori JL, Taleb Z, *Microchim. Acta*, 2010, **169**, 187-193.

22 A. Ballesteros-Gomez, M. D. Sicilia, *Anal. Chim. Acta*, 2010, **677**, 108–130.

23 E. Yılmaz, M. Soylak, *Talanta*, 2014, **126**, 191-195.

24 C.Z. Katsaounos, D.L. Giokas, A.G. Vlessidis, E.K. Paleologos, M.I. Karayannis, *Sci. Total Environ*. 2003, **305**, 157-167.

25 A. S. Yazdi, *TrAC Trends in Anal. Chem.,* 2011, **6**, 918–929.

26 N. P. Petridis, V. A. Sakkas, T. A. Albanis, *J. Chromatogr*., 2014, **1355A**, 46–52.

27 N. Jalbani, M. Soylak, *Ecotox. Environ. Safe*, 2014, **102**, 174–178.

28. M. Costas-Rodriguez, F. Pena-Pereira, Method Development with Miniaturized Sample Preparation Techniques, in: Miniaturization in sample preparation, Chapter, 6De Gruyter Open, 2014,.

29. C. Stalikas, Y. Fiamegos, V. Sakkas, T. Albanis, *J. Chromatogr*., 2009, **1216A**, 175–189

30 A. Niazi, N. Khorshidi, P. Ghaemmaghami, *Spectrochim. Acta, 2*015, **135A**, 69–75.

31 P. X. Baliza, L.S. G. Teixeira, V. A. Lemos, *Microchem. J.,* 2009, **93**, 220–224.

32 M. R. Jamali, B. Soleimani, R. Rahnama, S. H. A.Rahimi, *Arab. J. Chem*., 2012, DOI: 10.1016/j.arabjc.2012.08.004.

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

34 M.A. Karimi, S.Z. Mohammadi, A. Hatefi-Mehrjardi, A. Mohadesi, J. Yarahmadi, J. Anal. Sci. Techn., 2015, **6,** 25. DOI 10.1186/s40543-015-0065-2

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

36 S.G. Ozcan, N. Satiroglu, M. Soylak, Food Chem. Toxicol., 2010, **48,** 2401-2406.

37 M.K. Moftakhar, M.R. Yaftian, A. Zamani, J. Anal. Chem., 2015, **70,** 1085–1091.

38. S. Saracoglu, M. Soylak, L. Elci, Trace Elemen. Electroly., 2001, **18,** 129-133.

39 D. Bakircioglu, N. Topraksever, Y.B. Kurtulus, Food Anal. Methods, 2015, **8,** 2178–2184.

40 M. Soylak, Y. Akkaya, Trace Elemen. Electroly., 2002, **19,** 100-104.

41 H.R. Rajabi, S. Razmpour, Spectrochim. Acta, 2016, **153A,** 45-52.

42 G. Pavlovska, T. Stafilov, K. Čundeva, J. Environ. Sci. Health, 2015, **50A,** 1386-1393.

43 M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Environ. Mon. Assess., 2007, **127,** 169-176).

44 H. Jiang, Y. Qin, B. Hu, *Talanta*, 2008, **74**, 1160–1165.

45 M. Rayabi, S. Asemipour, B. Barfi, M.R. Jamali, M. Behzad, *J. Mol. Liq.*, 2014, **194**, 166–171.

46 S. Saracoglu, M. Soylak, D. Cabuk, Z. Topalak, Y. Karagozlu, *J. AOAC Int.,* 2012, 95, 892-896.

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

48 IUPAC, *Spectrochim. Acta,* 1978, **33B,** 241.

49 S. Jafarvand, F. Shemirani, *Microchim. Acta*, 2011, **173**, 353-359.

50 S.R. Yousefi, S.J. Ahmadi, Microchim *Acta*, 2011, **172**, 75–82.

51 Z.A. Alothman, M.A. Habila, E. Yilmaz, N.M. Al-Harbi, M. Soylak, Int. J. Environ. Anal. Chem. (2015) in press, DOI: 10.1080/03067319.2015.1090568

Figure Captions

Fig. 1 Pareto chart for the significance of response of the variables: **P:** pH, **D:** 1-decanol volume, **L:** Ligand volume, **T:** THF Volume, **C:** Centrifugation time.

Fig. 2 Three dimension surface response for % recovery of Co(II) **(a).** Interaction D (µL)-L (µL), **(b).** T (µL)-D (µL) and, **(c).** pH-D (µL).

Fig. 3 The Effect of sample volume on the recovery of Co. (Experimental conditions: pH 6; the volume of DDTC (0.1 %): 300 µL; the volume of 1-decanol 125 µL; the volume of THF: 450 µL; Centrifugation time 8 min.; n=3).

Fig. 1

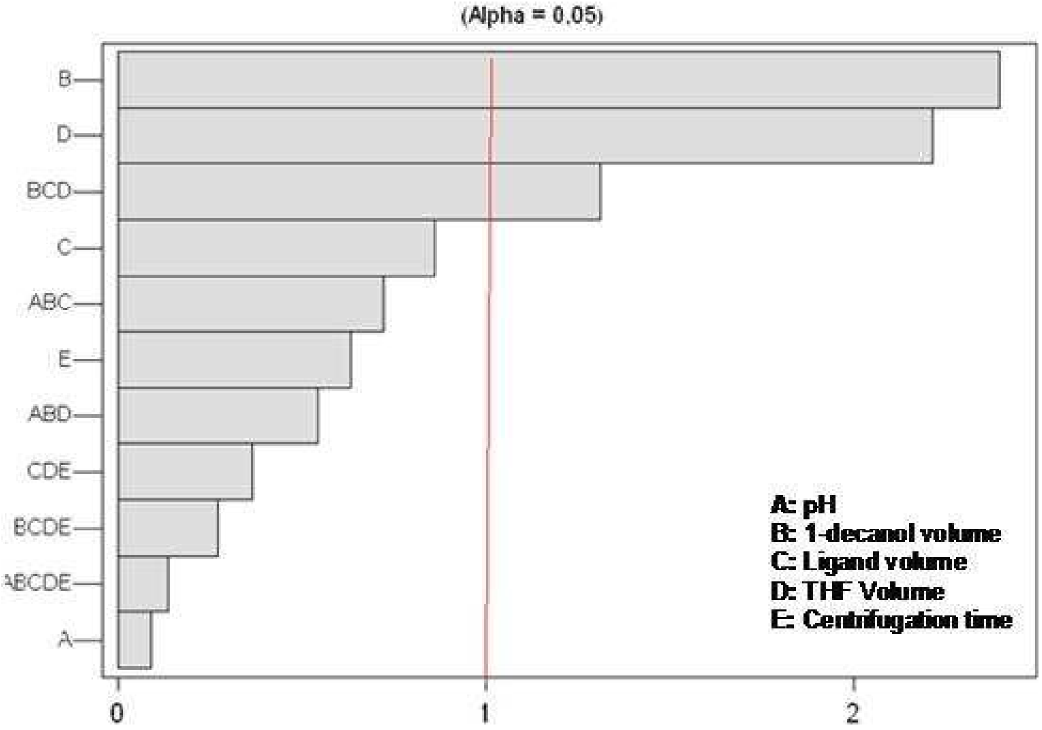
(Alpha = 0.05)
B
D
BCD
C
ABC
E
ABD
CDE
BCDE
ABCDE
A
A: pH
B: 1-decanol volume
C: Ligand volume
D: THF Volume
E: Centrifugation time
0
1
2

Fig. 2a

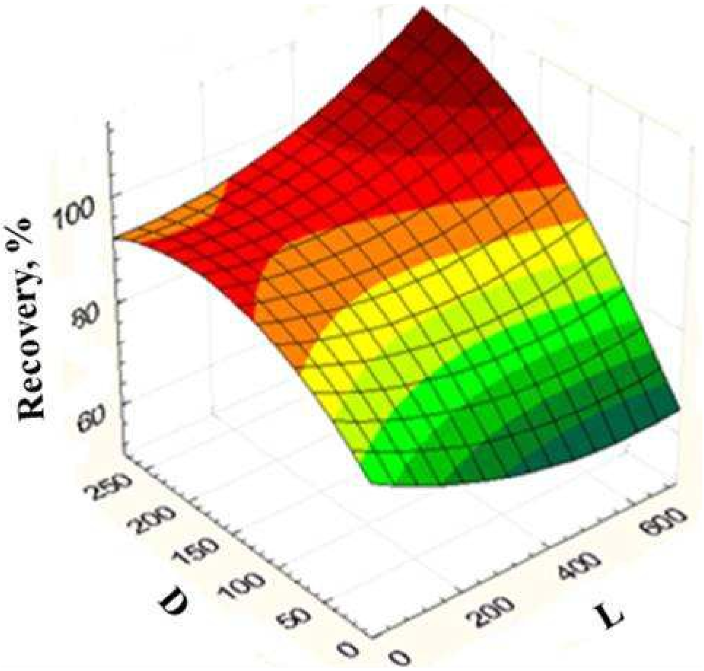

Fig. 2b

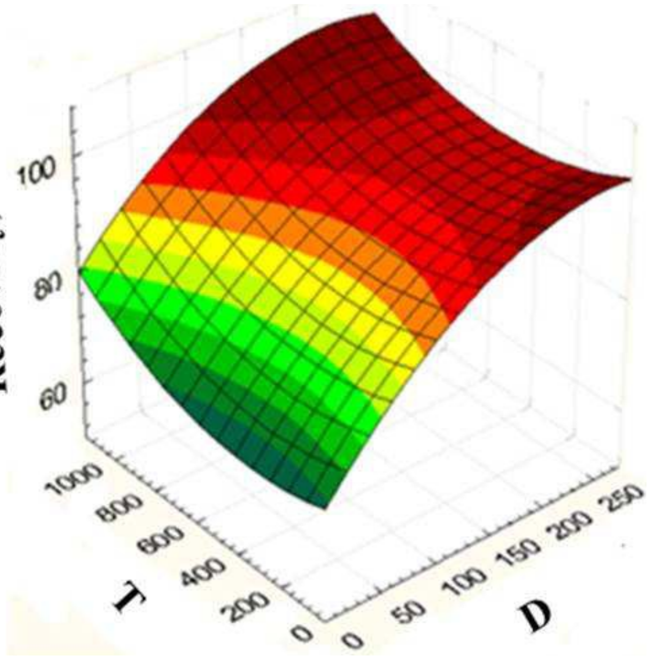

Fig. 2c

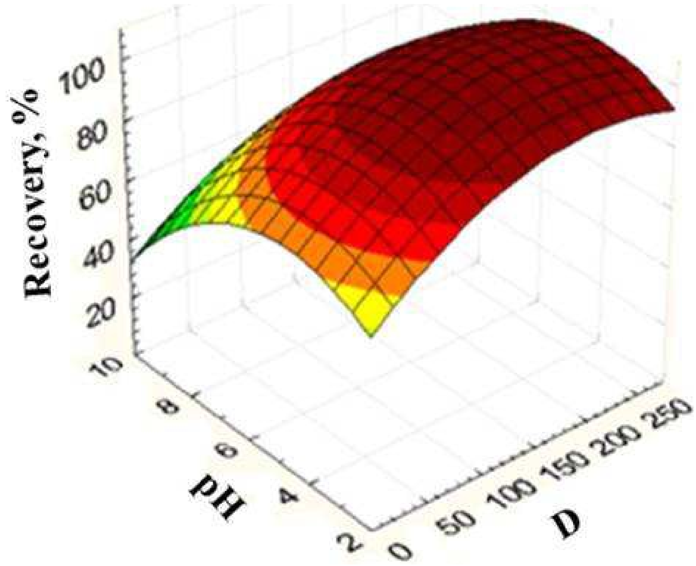

Fig. 3

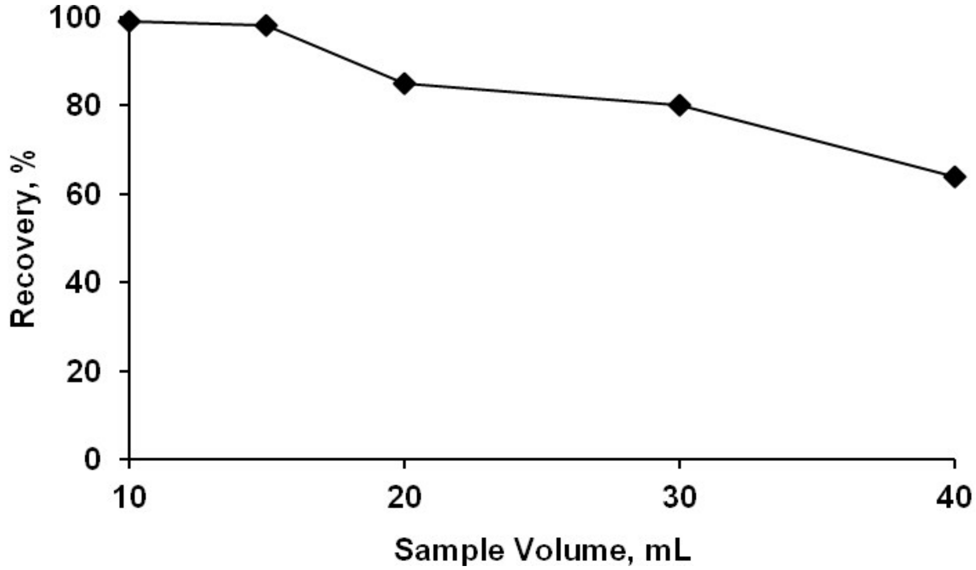

Table 1 Variable and levels used for the Plackett–Burman designs in the factorial design.

Parameters	Symbols	Variable Levels	
		Low (-)	**High (+)**
pH	P	2	8
Volume of 1-decanol (µL)	D	50	200
Volume of Ligand (% 0.1, µL)	L	50	500
Volume of THF (µL)	T	100	800
Centrifugation time (min.)	C	2	10

Table 2 Plackett-Burman experimental design (PBD) and the results of Co recovery

Study Number	P	D	L	T	C	Recovery, %
1	+	-	-	-	+	97
2	+	+	-	-	-	87
3	+	+	+	-	-	83
4	+	+	+	+	-	83
5	-	+	+	+	+	74
6	+	-	+	+	+	82
7	-	+	-	+	+	60
8	+	-	+	-	+	93
9	+	+	-	+	-	72
10	-	+	+	-	+	88
11	-	-	+	+	-	74
12	+	-	-	+	+	92
13	-	+	-	-	+	91
14	-	-	+	-	-	94
15	-	-	-	+	-	105
16	-	-	-	-	-	106

Table 3 Central 2^{3+} orthogonal composite design (n = 3) for pH (P), the volume of 1-decanol (D), the volume of ligand (L) and volume of THF (T).

Study Number	A (P)	B (D)	C (L)	D (T)	Recovery, %
1	${}_{a}P^{2}$	${}_{b}D^{2}$	${}_{c}L^{2}$	${}_{d}T^{2}$	100
2	-	-	-	-	93
3	+	-	-	-	81
4	-	+	-	-	98
5	+	+	-	-	95
6	-	-	+	-	81
7	+	-	+	-	63
8	-	+	+	-	103
9	+	+	+	-	91
10	-	-	-	+	88
11	+	-	-	+	73
12	-	+	-	+	104
13	+	+	-	+	80
14	-	-	+	+	80
15	+	-	+	+	80
16	-	+	+	+	104
17	+	${}_{b}D^{3}$	+	+	91
18	${}_{a}P^{1}$	${}_{b}D^{2}$	${}_{c}L^{2}$	${}_{d}T^{2}$	105
19	${}_{a}P^{2}$	${}_{b}D^{1}$	${}_{c}L^{2}$	${}_{d}T^{2}$	0
20	${}_{a}P^{2}$	${}_{b}D^{4}$	${}_{c}L^{2}$	${}_{d}T^{2}$	105
21	${}_{a}P^{2}$	${}_{b}D^{2}$	${}_{c}L^{1}$	${}_{d}T^{2}$	0
22	${}_{a}P^{2}$	${}_{b}D^{2}$	${}_{c}L^{3}$	${}_{d}T^{2}$	104
23	${}_{a}P^{2}$	${}_{b}D^{2}$	${}_{c}L^{2}$	${}_{d}T^{1}$	0
24	${}_{a}P^{2}$	${}_{b}D^{2}$	${}_{c}L^{2}$	${}_{d}T^{3}$	104

${}_{a}P^{1}$=2, ${}_{a}P^{2}$=6, ${}_{b}D^{1}$=0, ${}_{b}D^{2}$=125, ${}_{b}D^{3}$=200, ${}_{b}D^{4}$=275, ${}_{c}L^{1}$=0, ${}_{c}L^{2}$=300, ${}_{c}L^{3}$=700, ${}_{d}T^{1}$=0, ${}_{d}T^{2}$=450, ${}_{d}T^{3}$=1150.

Table 4 Tolerance limits of some coexisting ions (pH 6; the volume of DDTC (0.1 %): 300 µL; the volume of 1-decanol 125 µL; the volume of THF: 450 µL; centrifugation time 8 min.; n=3).

Matrix Ions	Added as	Concentration, mgL^{-1}	Recovery, %
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	2000	101 ± 3
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	2000	103 ± 4
K^{+}, Cl^{-}	KCl	2500	102 ± 2
Na^{+}	$NaNO_3$	2000	94 ± 2
SO_4^{2-}	Na_2SO_4	2000	102 ± 3
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	20	105 ± 4
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	10	93 ± 2
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	20	101 ± 2
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	20	99 ± 2
Ni^{2+}	$Ni(NO_3)_3{\cdot}6H_2O$	10	96 ± 4

Table 5 Addition/Recovery test for Co(II) for cereal samples (pH 6; the volume of DDTC (0.1 %): 300 µL; the volume of 1-decanol 125 µL; the volume of THF: 450 µL; centrifugation time 8 min; n=5).

Samples	**Added** **µg**	**Found[a]** **µg**	**Recovery** **(%)**
Vetch	0	0.35 ± 0.02	-
	1	1.29 ± 0.02	96
	2	2.36 ± 0.05	100
Wheat	0	0.37± 0.03	-
	1	1.31 ± 0.03	96
	2	2.32 ± 0.03	98
Lemon-flavored powdered beverage	0	BDL[b]	-
	1	0.94 ± 0.06	94
	1.5	1.39 ± 0.07	93

[a] Mean ± standard deviation

[b] BDL= Below the detection limit.

Table 6 The analysis results for certified reference materials (pH 6; the volume of DDTC (0.1 %): 300 µL; the volume of 1-decanol 125 µL; the volume of THF: 450 µL; centrifugation time 8 min; n=5).

Certified Reference Material	Certified value	Found	Recovery (%)
TMDA-53.3 Water - Trace Elements, (mg L^{-1})	0.252	0.258 ± 0.013[a]	102
TMDA-64.2 Water-Trace Elements, (mg L^{-1})	0.253	0.260 ± 0.009[a]	103
SPS-WW2 Waste Water-Trace Metals, (mg L^{-1})	0.300	0.310 ± 0.010[a]	103
Oriental Basma Tobacco Leaves (INCT OBTL-5), (mg kg^{-1})	0.981	1.019 ± 0.002[a]	104
Scallion (Salad Onion), (NCS ZC73033), (mg kg^{-1})	0.59 ± 0.04	0.61 ± 0.03	103

[a] Mean ± standard deviation

Table 7 The determination of cobalt in cereal, fruit and powdered beverage samples (pH 6; the volume of DDTC (0.1 %): 300 μL; the volume of 1-decanol 125 μL; the volume of THF: 450 μL; centrifugation time 8 min; n=5).

Samples	**Found, μg g^{-1}**
Green Lentils	1.68 ± 0.16[a]
Corn	5.32 ± 0.04
Barley	1.32 ± 0.12
Cherry-flavored powdered beverage	BDL[b]
Rosehip-flavored powdered beverage	BDL
Vibirnum opulus-guelder rose	BDL
Grape	BDL
Plum	BDL

[a] Mean ± standard deviation

[b] BDL= Below the detection limit.

Table 8 Comparison of analytical features of the developed method with other microextraction method.

Analytical Technique	Chelating reagent / Extraction phase	Matrix	EF / PF[a]	LOD [b] (µg L^{-1})	RSD[c] (%)	Ref
DLLME-FAAS	Br-TAO/ methanol/ carbon tetrachloride	Water	16	0.9	2.3-5.8	29
SFODME-GFAAS	PAN/1-undecanol	Water	502	0.4	4.6	12
ISFME-FAAS	5-Br-BADAP /[Hmim][BF4]/$NaPF_6$	Water	50	0.97	2.4	30
DLPME- GFAAS	PAN /acetone/carbon tetrachloride	Water, Rice	101	0.021	7.5	44
UA-IL-ME-FAAS	H_2L/[HMIM][PF_6] /acetone	Water	48-56	1.9-4.4	1.8–3.8	45
Ss-ME -FAAS	PAN/decanoic acid/THF	Water	58	4.2	2.1-3.8	49
Ss-ME -FAAS	PAN /[Hmim][PF6]/ etanol	Water	118	0.1	2.9	50
Ss-ME -FAAS	N-Benzoyl-N,N-diisobutylthiourea/1-decanol/THF	water samples	40	1.29	3.2	51
Ss-ME-FAAS	DDTC/1-decanol/THF	Water, Cereals, Fruit, Powdered beverage	30	1.89	2.4	This work

[a] Enrichment factor, [b] Limit of detection, [c] RSD Relative standard deviation, FAAS: Flame atomic absorption spectrometry, GFAAS: Graphite furnace atomic absorption spectrometry, DLLME: Dispersive liquid–liquid microextraction, SFODME: Solidified Floating organic organic drop microextraction, ISFME: In situ solvent formation microextraction, DLPME: Dispersive liquid phase microextraction, UA-IL-ME: ultrasonic assisted-ionic liquid based-liquid–liquid microextraction, Ss-ME: Supramolecular solvent based microextraction.