

Cloud Point Extraction Using Tergitol TMN-6 of Gold() in Real Samples by Flame Atomic Absorption Spectrometry Determination

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Summary: A simple, safe and rapid method on the basis of cloud point extraction(CPE) with tergitol TMN-6 had been used for the preconcentration and extraction of gold(Au) ion in selenium reduction solution sample prior to flame atomic absorption spectrometry (FAAS).Pyrrolidine dithio fromic acid salt(PDFAS)which was regarded as a selective complexing agent could formed stable Au-complex with Au ion, and Au-complex could be extracted by TMN-6 at a short time. Some influencing factors such as sample pH, concentration of TMN-6, concentration of PDFAS and the effect of foreign ions were further researched .Under the optimum conditions, the limit of detection(LOD) was $1.3\mu\text{g L}^{-1}$,the calibration graph was linear in the range of 0-500 $\mu\text{g/L}$ and the relative standard deviation(RSD%) was 2.0%(n=8). The CPE method had been shown to be a useful and effective methodology for the separation of Au, with a preconcentration factor of 30. The recoveries of the spiked Au() ions were got in the range 95–103%.

Keywords: Cloud point extraction; Pyrrolidine dithio fromic acid salt; Gold; Flame atomic absorption spectrometry; Tergitol TMN-6

Introduction

Gold is one of valuable elements in the earth. The average concentration of Au in geological body in general is in the range of 1ng/g-4ng/g.The average concentration of oceans, rivers, lakes and other water bodies in general are in the range of 0.05-0.2ng/ml [1]. Gold products are widely used in petrochemical, pharmaceutical, electronic and nuclear power industries etc. When the environment of gold reaches a certain concentration, it will be harm for the biological body [2]. In view of the above mentioned the rare characteristics of gold and the damage to the environment of gold, it is necessary to adopt certain means and measures in the detection and treatment of gold in industrial waste water and then further recycling.

Today, the removal/preconcentration method for determination of gold include: metal replacement method [3], solvent extraction [4, 5], ion exchange method [6, 7] and electrochemical methods [8]. However, these methods have high operating costs, and some treatment effect is ineffective at low concentrations of metal ions, and they are difficult to realize industrialization. Therefore, a simple, safe and efficient separation technique for gold species is necessary.

CPE as an alternative to traditional

liquid-liquid extraction had attracted a lot of attention .The CPE was used to removing lead, cobalt and copper in water by Demirhan Citak in 2010 [9]. The traditional separation methods such as liquid liquid extraction which required a lot of time and high purity toxic organic reagent [10].CPE was a kind of green separation and enrichment methods, and there were some advantages :(1) The surface active agent was cheap and low toxicity; (2) CPE had simple operation; (3) the CPE had a higher enrichment factor. CPE could made the surface activity produced turbid phenomenon and led to phase separation by changing the temperature, concentration and other external factors, at this time, the temperature was regarded as the cloud point temperature, and this phenomenon was called the cloud point phenomenon. In view of the aforementioned advantages, CPE had been widely used for the preconcentration of ions as a pre-processing method to the determination of ions by inductively coupled plasma atomic emission spectrometry ICP-AES [11-13], atomic absorption spectrometry (AAS) [14-16], ultraviolet visible spectrophotometry(UV) [17] and catalytic kinetic spectrophotometry(CK) [18].

Compared with other surfactant heads,TMN-6 reported in literature has the following

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advantages:(1).It was cheap, a non-ionic surfactant and environment -friendly;(2).It had high enrichment factor;(3).The time of separation and preconcentration was short. So it was effective surfactant, and it had been used to extract metal ions in many fields. The cloud point (CP) of TMN-6 was roughly 55°C ,and it was also heterogeneous alcohol ethoxylate surfactant.

In this research, PDFAS was used as a selective complexing agent, TMN-6 was investigated as the cloud point extractant in the separation of the Au(III) ions and the determination of Au(III) ions by FAAS. According to our knowledge, TMN-6 being regarded as chelating agent for CPE of Au(III) had not been widely used in literature. Several factors which may affected the extraction and determination procedures were discussed in below.

Experimental

Apparatus

Stock standard solution (1.0mg/mL) of Au was obtained from the Yunnan College of Metallurgy Vocational(Yunnan, China).The buffer solution was composed of acetic acid and sodium acetate. Acetic acid and sodium acetic were purchased from Tianjin Chemical Reagent Factory Three (Tianjin, China) and Tianjin City Dongsheng Chemical Reagent Factory (Tianjin, China),and they were analytical grade.TMN-6 was analytical grade and purchased from Shanghai Bo'ao Biologica Technology Co.,(Shanghai, China). PDFAS was analytical grade and purchased from Nanjing firstly Technology Co., (Nanjing, China).In this study, all the reagents were mostly analytical grade.

A vortex instrument,purchased from Anhui USTC Zonkia Scientific Instruments Co., (Anhui, China),was used to mix solution and a centrifuge instrument which was bought from Shanghai Khan novo Instrument Co.,(Shanghai, China) was used to carried out the phase separation process. Flame atomic absorption spectrometer, purchased from Rui Sheng Technology Co.,(Shimadzu, Japan), was used for the determination of the amount of Au(III).

Experiment Process

For the cloud point extraction experiments, aliquots of working standard solution of Au(III),2 ml pH=4.0 buffer solution, 1mL TMN-6(10% v/v), 1ml APDC (0.1g/L) solution were placed in a 10mL

centrifuge tube. And the centrifuge tube was vortex-mixed for 3min. Then, the mixtures solution were diluted to10.0mL with deionized water, and it was heated in the water-bath at 45 for 30min.A centrifugation was used to separate the cloudy solution at 3000rpm for 10min.Then,the aqueous phase was removed from the centrifuge tube by a syringe. The surfactant rich phase was diluted with nitric acid to 500ul and the content of Au(III) were determined by FAAS.

Results and Discussion

Effect of Surfactant Concentration on the CPE of Au

Fig. 1 showed that the different surfactant concentration had effect on the CPE of TMN-6. In the curve below, TMN-6 existed in the form of micelles in solution (one-phase) whereas in the curve above showed that two-phase exist. The results were showed in Fig. 1, when the concentration of TMN-6 was 0.06% (v/v), the highest cloud point temperature of TMN-6 was 74.1 . When the concentration was more than0.06% (v/v),the temperature reduced by increasing the TMN-6 concentration. When TMN-6 concentration was 5% (v/v), the cloud point temperature of the mixed solution was the lowest (34.2 °C).

Effect of pH on the CPE of Au

The pH value had an important effect on cloud point extraction of metal ion, it mainly affected on the reaction of metal ions and chelating agents and then affected on the extraction rate. In the same condition, the experiment was studied the pH value in the range of 2.0–12.0 and the results were showed in Fig. 2. According to the results, the maximum absorbance of Au(☞)was reached when pH4.So pH4 was chosen as the optimal pH value for this experiment.

Effect of Tergitol TMN-6 concentration on CPE of Au()

The amount of surfactant affected on CPE by the following aspects: (1)Extraction rate; (2) Enrichment volume phase; (3) The process of phase separation. In this experiment, TMN-6 concentration in the range of 0.05% (v/v) to 0.2%(v/v) were researched on the impact of CPE (Fig. 3).The results showed that the absorbance increased with increasing the TMN-6 concentration up to 0.1% (v/v) because the TMN-6 concentration in this range increasing was

propitious to metal ions and chemical reagent to form chelate complexes. While the absorbance reduced by increasing the TMN-6 concentration afterwards, the results showed that TMN-6 concentration increasing led to surfactant metal ion phase enrichment factor reducing. So a concentration of 0.1% (v/v) of PDFAS was selected as the optimal concentration of TMN-6 for this experiment.

Effect of the PDFAS Concentration on CPE of Au()

In order to find more suitable APDC concentration, in this experiment, the concentration of PDFAS in the range of 0.5 mg L^{-1} to 10 mg L^{-1} were researched. The results were obtained in Fig. 4, and it showed that the absorbance increased by increasing the PDFAS concentration up to 1.5 mg L^{-1} and then remained constant afterwards. So in this experiment, a concentration of 1.5 mg L^{-1} of PDFAS was chosen as the optimal concentration of PDFAS for following determinations.

Effect of Coexisting Ions on CPE of Au()

According to the method of experiment

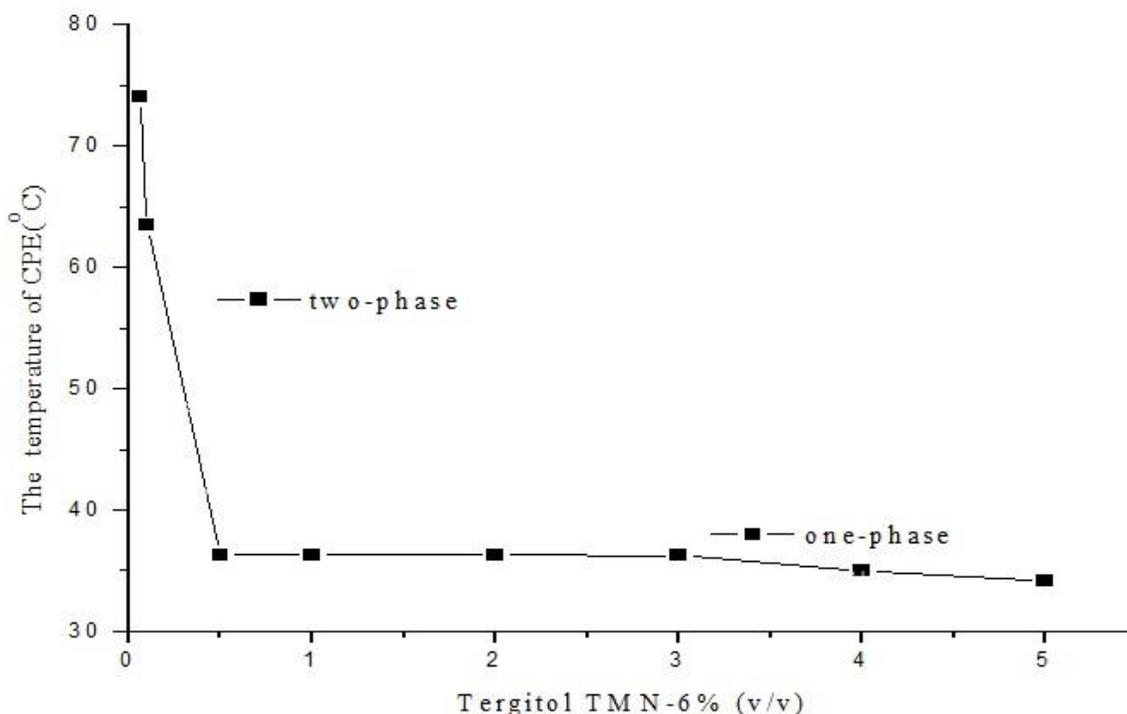


Fig. 1: Cloud point of TMN-6 solution as a function of surfactant concentration. Other experimental conditions were the concentration of TMN-6 was 5% (v/v) and the concentration of PDFAS was 0.1 g/L , the temperature was $45 \text{ }^{\circ}\text{C}$, the equilibrium time was 30 min, $\text{pH}=4$, respectively.

operating, the interference of coexisting ions test were carried out with 0.3 mg/L water samples. The results were obtained in Table-1. Coexisting ions, which were allowed, were showed in Table-1 when the relative error was less than 5%. The results showed that most common ions did not interfere the determination of Au().

Table-1: Effect of coexisting ions on determination of the content of gold(III).

Coexisting ions	Permissible limit (mg/L)	Recovery(%)
Cl ⁻	1000	98.9
K ⁺	1000	98.2
Mg ²⁺	1000	97.7
Na ⁺	1000	102
Ca ²⁺	1000	97
Cr ²⁺	800	97.8
Cd ²⁺ , Mn ²⁺	800	96.1
Ni ²⁺ , Zn ²⁺	800	97
Pb ²⁺	800	98
Fe ²⁺ , Fe ³⁺	750	95.7
Zn ²⁺	750	95.7
Cu ²⁺ , HCO ₃ ³⁻ ,	750	97.1
NO ₃ ⁻ , SO ₄ ²⁻ , Br ⁻ ,	750	97.3

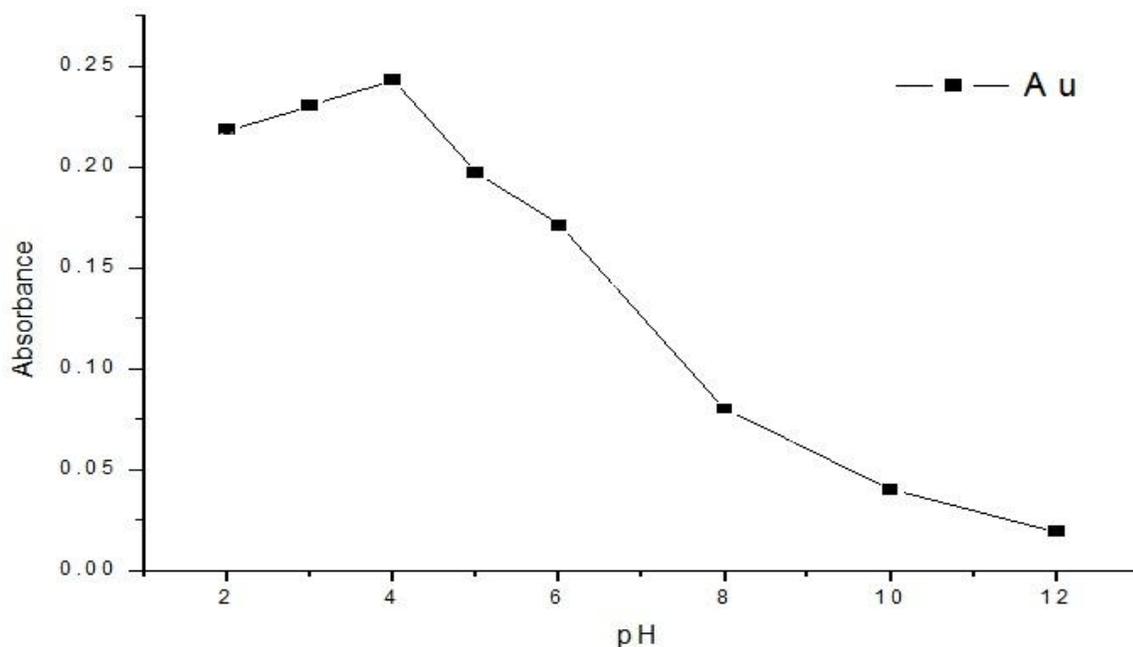


Fig. 2: Effect of pH on the cloud point extraction of Au. Other experimental conditions were the concentration of TMN-6 was 5% (v/v) and the concentration of PDFAS was 0.1g/L, the temperature was 45 °C, the equilibrium time was 30 min, respectively.

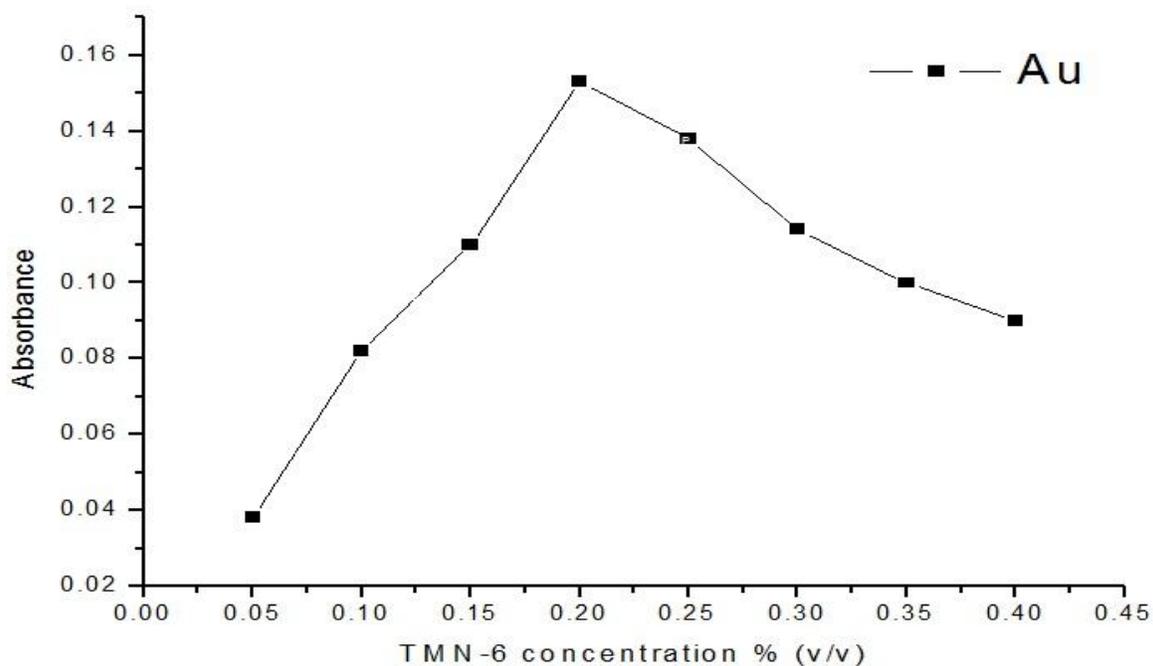


Fig. 3: Effect of Tergitol TMN-6 concentration on the cloud point extraction of Au. Other experimental conditions are concentration of PDFAS was 0.1g/L; equilibrium temperature: 45 °C; equilibrium time: 30 min; pH=4. Other experimental conditions were the concentration of PDFAS was 0.1g/L, the temperature was 45 °C, the equilibrium time was 30 min, pH=4, respectively.

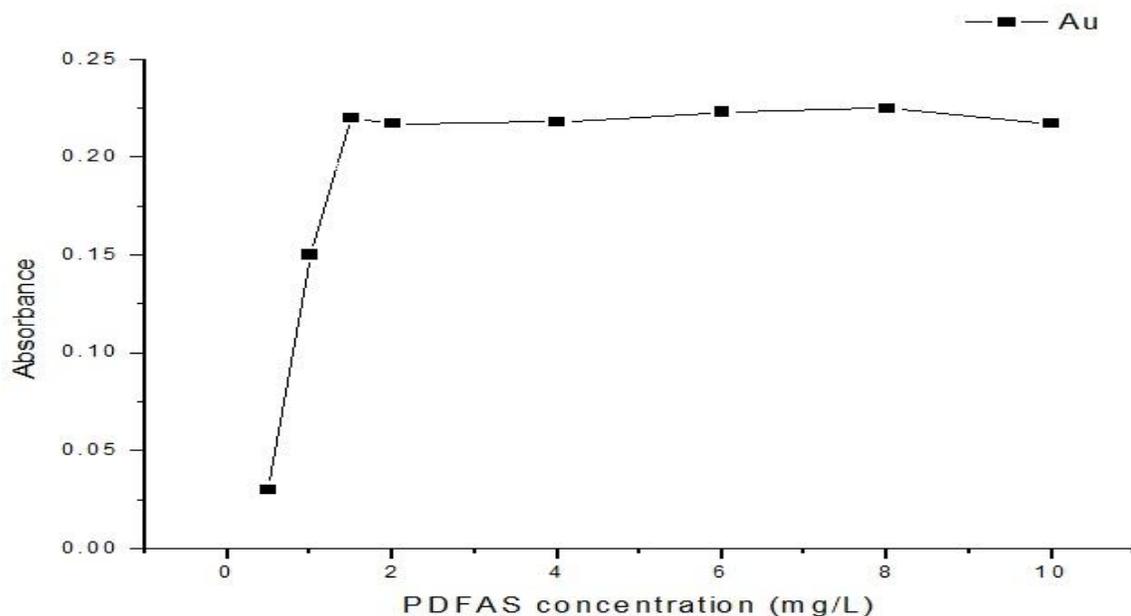


Fig. 4: Effect of the PDFAS concentration on the cloud point extraction of Au. Other experimental conditions were the concentration of TMN-6 was 5% (v/v), the temperature was 45 °C, the equilibrium time was 30 min, pH=4, respectively.

Table 2. Performance characteristics of CPE

Analyte	Enrichment factor	Linear range($\mu\text{g/L}$)	Regression equation	R^2	LOD	RSD(%)n=8
Au	30	1.0-500	$Y=0.13x+0.04$	0.995	1.3($\mu\text{g/L}$)	2.0

Table-3. The comparison of tergitol TMN-6 with other reagents

Reagents	Sample volume(mL)	Preconcentration time(min)	RSD(%) (n=8)	Injection Volume(mL)	LOD($\mu\text{g/L}$)	Preconcentration factor
TritonX-114	10	>10	3.2	5	7.0	10
CTAB	10	12	2.7	5	12	20
TritonX-100	10	>10	2.1	5	6.0	25
Tergitol TMN-6	5	10	2.0	1	1.3	30

Analytical Features

In the best conditions, the LOD was 1.3 $\mu\text{g L}^{-1}$, the calibration graph was linear in the range of 0-500 $\mu\text{g/L}$ and the RSD(%) was 2.0%(n=8), the regression equation was $Y = 0.13x + 0.04$, $R^2=0.995$. The results were showed in Table-2.

Comparison of Tergitol TMN-6 with other reagents

The characteristic data of the tergitol TMN-6 for the determination of Au() with other reagents were compared in this study. It can be seen from Table-3 that the tergitol TMN-6 had lower limit of detection and preconcentration time shorter compared with other reagents with only 5mL of the sample solution, and preconcentration factor was higher than other reagents. It was suitable for

determination of trace amounts of Au() in real samples.

Analysis of Real Samples

The experiment was examined to determine Au() ion in real samples including Industrial waste water and selenium reduction solution, which were all from Kunming. A certain quality of water samples, 5ml nitric acid and 2ml perchloric acid were placed on a heating plate to conduct digestion. Then, all the water samples which were spiked with Au() standard solution at different concentration levels were determined. The results were showed in Table-4 and the recovery was 95% 103%. It indicated that the studied method applied to the analysis requirements of the determination of Au() in real samples.

Table-4: Result of determination of gold real samples.

Sample	Spiked($\mu\text{g L}^{-1}$)	Found($\mu\text{g L}^{-1}$)	Recovery(%)
Industrial waste water	0	Not detected	—
	10	8.7 \pm 0.2	99.0
	20	16.9 \pm 0.1	101.1
Selenium reduction solution	0	Not detected	—
	10	16.9 \pm 0.4	99.3
	20	32.8 \pm 0.2	104.3

Conclusion

A simple, safe and rapid CPE methodology with tergitol TMN-6 had been studied in this test. PDFAS as a selective complexing agent and Tergitol TMN-6 as a non-ionic surfactant were applied to the process of cloud point extraction with low LOD and good results. In this experiment, the CPE methodology had been prosperous used in the determination of trace Au (Au^{3+}) in real samples.

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References

- J. A. Omgbu, N. S. Ohochuku, V. Iweanya and E. M. Obaseki, Coconut palm (Cocos nucifera) Husk as a Potential Adsorbent for Lead, Cadmium and Zinc Ions in Industrial Waste Effluents, *Pak. J. Sci. Ind. Res.*, **40**, 41 (1998).
- S. M. Hasany and R. Ahmad, Removal of Traces of Silver Ions from Aqueous Solutions Using Coconut Husk as a Sorbent, *Sep. Sci. Technol.*, **39**, 3509 (2004).
- F. B. Li and X. Z. Li, Photocatalytic Properties of Gold/Gold ion-Modified Titanium Dioxide for Waste Water Treatment, *Appl. Catal. A-Gen.*, **228**, 15 (2002).
- B. T. B. Maria, D. Edward and L. Wojciech, Gold Cyanide Ion Electroreduction on Gold Electrode, *J. Electroanal. Chem.*, **99**, 341 (1979).
- J. Lee, L. P. Jayathiklaka, S. Gupta, J. S. Huang and B. S. Lee, Gold Ion-Angiotensin Peptide Interaction by Mass Spectrometry, *J. Am. Soc. Mass Spectr.*, **23**, 942 (2012).
- M. I Setyawati, J. P. Xie and D. T. Leong, Phage Based Green Chemistry for Gold Ion Reduction and Gold Retrieval, *ACS Appl. Mater. Inter.*, **6**, 910 (2014).
- M. C Salvadori, F. S Teixeira, L.G Sgubin, W. W. R Araujo, R. E Spirin and M. Cattani, Gold Ion Implantation into Alumina Using an "Inverted ion source" configuration, *Rev. Sci. Instrum.*, **85**, 02B502 (2014).
- N. K. Badri and S. Natarajan, MycocrySTALLIZATION of Gold Ions by the fungus *Cylindrocladium Floridanum*, *World J. Microb. Biot.*, **29**, 2207 (2013).
- D. Citak and M. Tuzen, 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 Chem. Toxicol.*, **48**, 1399 (2010).
- Naeemullah, M. Tuzen, T. G. Kazi, D. Citak and M. Soylak, Pressure-Assisted Ionic Liquid Dispersive Microextraction of Vanadium Coupled with Electrothermal Atomic Absorption Spectrometry, *J. Anal. At. Spectrom.*, **28**, 1441 (2013).
- C. Mico, L. Recatala, M. Peris and J. Sanchez, Assessing Heavy Metal Sources in Agricultural Soils of an European Mediterranean Area by Multivariate Analysis, *Chemosphere*. **65**, 863 (2006).
- T. Chen, X. M. Liu, M. Z. Zhu, K. L. Zhao, J. J. Wu, J. M. Xu, P. M. Huang, Identification of Trace Element Sources and Associated Risk Assessment in Vegetable Soils of the Urban-Rural Transitional Area of Hangzhou, China, *Environ. Pollut.*, **151**, 67 (2008).
- V. Boonamnuayvitaya, C. Chaiya, W. Tanthapanichakoon, S. Jarudilokkul, Removal of Heavy Metals by Adsorbent Prepared from Pyrolyzed Coffee Residues and Clay, *Sep. Purif. Technol.* **35**, 11 (2004).
- A. Facchinelli, E. Sacchi and L. Mallen, Multivariate Statistical and GIS-Based Approach to Identify Heavy Metal Sources in Soils, *Environ. Pollut.*, **114**, 313 (2001).
- F. A. Lopez, M. I. Martin, C. Perez, A. Lopez-Delgado and F. J. Alguacil, Removal of Copper Ion from Aqueous Solution by a

- Steel-Making by-Product, *Water Res.*, **37**, 3883 (2003).
16. D. A. Sousa, E. Oliveira, M. C. Nogueira, B. P. Espósito, Development of a Heavy Metal Sorption System Through the P=S Functionalization of Coconut (*Cocos nucifera*) Fibers, *Bioresource Technol.*, **101**, 138 (2010).
17. S. M. Hasany, R. Ahmad, The Potential of Cost-Effective Coconut Husk for the Removal of Toxic Metal Ions for Environmental Protection, *J. Environ. Manage.*, **81**, 286 (2006).
18. S. R. Shukla, R. S. Pai and A. D. Shendarkar, Adsorption of Ni(II), Zn(II) and Fe(II) on Modified Coir Fibres, *Sep. Purif. Technol.*, **47**, 141 (2006).