International Journal of Advanced Technology in Engineering and Science
Vol. No.3, Special Issue No. 01, September 2015
www.ijates.com
ijates
ISSN 2348 - 7550

A REVIEW ON APPLICATION OF HYPHENATED FLOW INJECTION SYSTEM FOR DETERMINATION OF HEAVY METAL IONS IN WATER SAMPLES

Shelja Tiwari[1], Niharika Sharma[2], Reena Saxena[3]

[1,2,3]*Department of Chemistry, Kirori Mal College, University of Delhi, (India)*

ABSTRACT

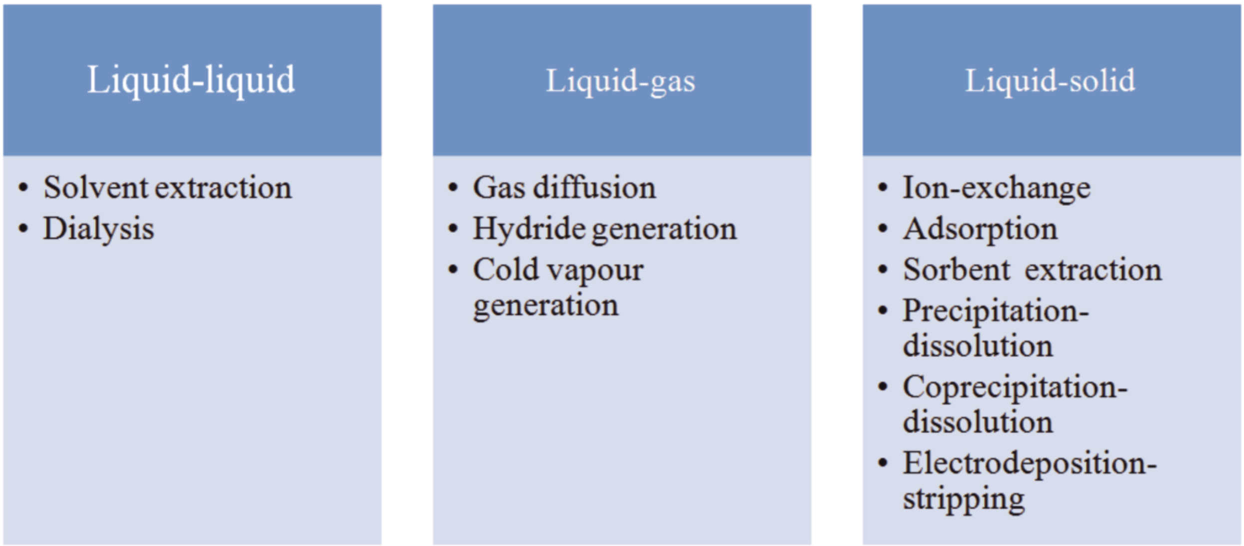
The presence of heavy metal ions even in trace amounts pose an imminent danger to environment and once these enter the food chain they become threat for both mammals and for aquatic organisms. The industrial effluents are one of the major reasons responsible for the contamination of environmental system. The direct determination of trace metal ions using a singular detection technique is a challenging task. Flow injection analysis has become a popular tool for solving analytical problems. The flow injection system is simple, fast and a useful technique which is applied in quantitative chemical analysis. This offers many advantages like minimum reagent consumption, reproducible results, and high sampling frequency. The system is automated and can be easily coupled to many analytical techniques. The aim of this review is to discuss various methods based on the hyphenation of flow injection system with detection techniques for the determination of heavy metal ions in different water samples.

Keywords: Heavy Metal Ions, Flow Analysis, Hyphenation, Flow Injection

I. INTRODUCTION

Heavy metal toxicity is one of the major environmental problems. The toxicity of these metals is associated to the fact that they are not important from biological aspect but their presence is harmful for proper functioning of human body. Due to their long existence in environment the treatment of these ions has become extremely important. Few of these are capable of replacing essential metal ions in human body [1]. The build-up of heavy metal ions in soil has raise a serious concern in agricultural production as they adversely affects crop growth by interfering with the biochemical processes of the plants [2]. This is the reason that recently a lot of stress is put in developing methods for removal of these ions from wastewater. WHO has decided permissible limit for various metal ions in drinking water [3]. So far many spectrometric techniques have been extensively used for the detection of metal ions at trace levels. Electrothermal atomic absorption spectrometry (ETAAS) [4] and flame absorption spectrometry (FAAS) offers better selectivity and are cost effective. Inductively coupled plasma atomic optical spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) allows simultaneous determination of more than one element and also gives low detection limits [5]. Other than these techniques UV-Visible spectrophotometry (UV-Vis) [6] and Atomic fluorescence spectrometry (AFS) [7] have also been used for determination of metal ions. In spite of the several advantages associated to these techniques operational factors, matrix interferences reduce the effectiveness of these systems. The batch method of detection involves large volume of reagents and is also time consuming. In this method there is a risk of contamination too. These disadvantages can be overcome by introducing a step before the detection step which simultaneously allows the enrichment of metal ions such as hyphenation with flow injection preconcentration techniques. A ***hyphenated technique*** is developed by coupling or combining a separation technique with a spectroscopic technique. This technique involves various combinations like separation-separation, identification-identification or separation-identification. The advantages of hyphenation are better analysis, improved sensitivity and selectivity [8]. This technique is automated, fast, requires less volume of reagents, lowers the risk of contamination and can easily be coupled to various detection techniques [9]. The flow injection analysis was proposed by Ruzicka and Hansen in1975 [10].

Flow injection (FI) systems are considered as a very important tool which enhances the ability of analytical techniques. The presence of microcolumn in the flow injection system provides better selectivity and sensitivity to the system after the optimising various flow and chemical variables. The FI separation methods can be differentiated on the basis of the type of interface across which the transfer is taking place. The types of separation systems are given in Fig. 1 [11].



Liquid-liquid	Liquid-gas	Liquid-solid
• Solvent extraction • Dialysis	• Gas diffusion • Hydride generation • Cold vapour generation	• Ion-exchange • Adsorption • Sorbent extraction • Precipitation-dissolution • Coprecipitation-dissolution • Electrodeposition-stripping

Fig.1 Classification of FI separation techniques

The FI separation technique in conjunction with a detection technique provides a mean to overcome the difficulties and enhances the selectivity of a singular detection technique. Various analytical techniques hyphenated to FI have been routinely used for the determination of metal ions in different environmental matrices (Fig. 2). *The aim of this review is to discuss latest research based on the hyphenation of FI system with various detection techniques*.

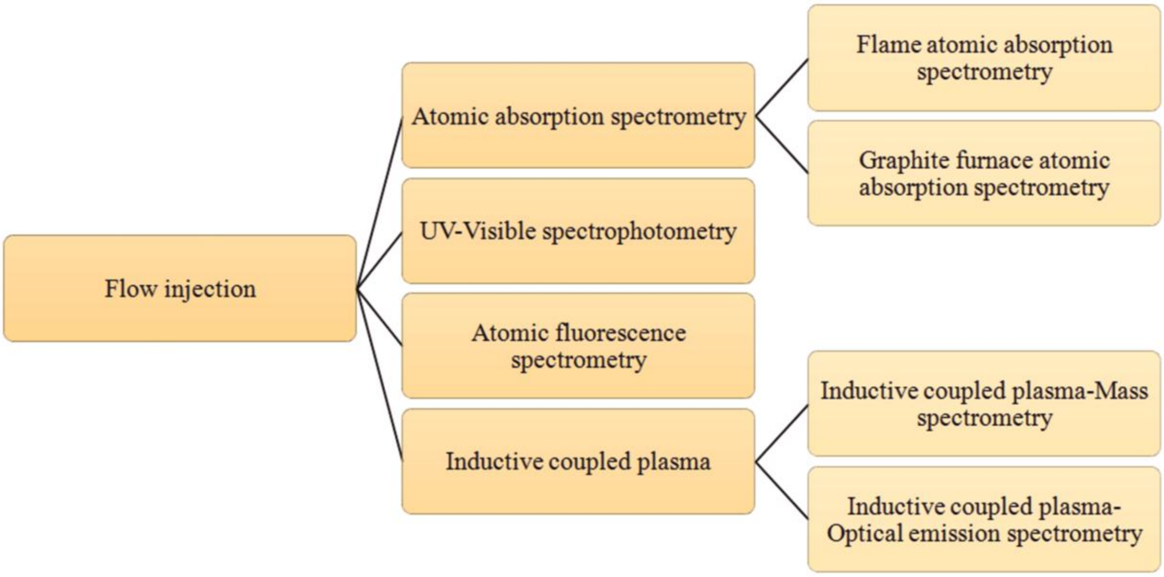


Fig. 2 Hyphenation of Flow Injection with Different Analytical Techniques

II. FLOW INJECTION SYSTEM HYPHENATED TO ATOMIC ABSORPTION SPECTROMETRIC TECHNIQUES

Atomic absorption spectrometry is a widely used technique for the quantitative determination of metal ions at trace levels. The sample here is generally volatilized either by furnace or by flame. In this a specific wavelength of light is adsorbed by an element which corresponds to the energy required to promote the electrons from one energy level to another higher level.

2.1 Fi-Faas

The flame atomic absorption spectrometer (FAAS) comprises a flow-through detector which fed the sample directly into the nebulizer-burner system via suction process. The characteristics of the FAAS system can be significantly enhanced by introducing sample by the FI mode. The hyphenation of FI-FAAS leads to decrease in sample consumption and preconcentrates the analyte of interest. The other advantages associated to this coupled technique are lower time of analysis, removal of matrix ions at preconcentration stage, direct introduction of sample to nebulizer from FI system there by lowering the risk of contamination. Recently, several FI-FAAS systems have been proposed for heavy metal preconcentration in industrial water samples. Most of these methods generally use solid phase extractant as a method of preconcentration. In 2012, xylenol orange immobilized on Amberlite XAD-2 was used in a FI-FAAS system to perconcentrate cadmium in industrial water samples [12]. The method suggested here showed good results in terms of sensitivity, selectivity in comparison to other reported methods. Recently an Innovative flow injection flame atomic absorption spectrometric method was suggested for the determination of Cu(II) in industrial samples [13]. Amberlite XAD-2 modified with dithizone was used as a complexing agent. The reported system was very simple and was capable of detecting Cu(II) in presence of high concentration of interfering ions. The suggested method was automated and offered better sensitivity in terms of detection limit. This FI-FAAS method has been also exploited for the speciation of metal ions. The importance of this can be highlighted by the fact that for certain metal ions one of their oxidation state is considered to be essential while other can be harmful to living system. In this direction, a method for the speciation of chromium species was proposed using FI-FAAS [14]. This paper has described a system for the speciation and preconcentration of chromium species by synthesizing dithizone anchored Dowex Optipore L493 system. The suggested method was applied for the determination of both Cr(III) and Cr(VI) in industrial water samples. The reported method was fast and required very low volume of reagents and has offered better concentration efficiency as well. A schematic representation for the working of FI-FAAS preconcentration system is given in Fig. 3 [14]. Other than these many FI-FAAS systems have been recently developed for heavy metal preconcentration in different water samples [15, 16]. Various ion exchange resins can also be directly used in FI-FAAS system for the removal of metal ions [17]. It is not necessary to use polymeric support for preconcentration, many systems with silica [18, 19], alumina [20], nano materials [21] etc. has also been used with FI-FAAS system for heavy metal analysis in different water samples.

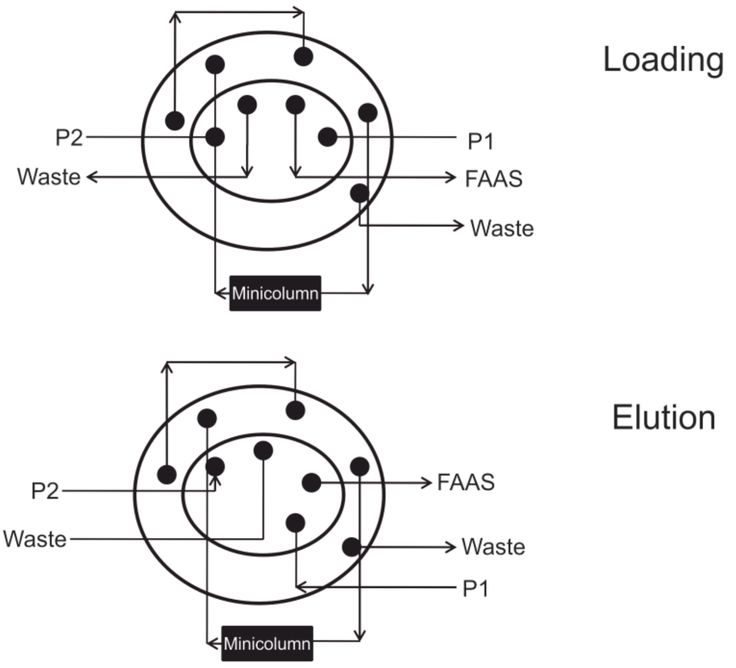


Fig.3 A Schematic Representation for the Working of FI-FAAS Preconcentration System

2.2 Fi-Gfaas

Graphite furnace atomic absorption spectrometry which is also known as Electrothermal Atomic Absorption Spectrometry is also a very sensitive spectroscopic technique. It is a single element technique used for trace metal analysis in various solid and aqueous samples. The coupling of FI system with GFAAS results in improvement in the overall performance of this technique in terms of sensitivity and selectivity [22]. A system was proposed for the preconcentration of palladium using chelating resin microcolumn [1,5-Bis(2-pyridyl)-3-sulphophenylmethylene thiocarbonohydrazide immobilized on an anion-exchange resin (Dowex 1 X8-200)] [23]. This paper has shown the advantages of hyphenated system over singular technique. A fully automated system without any complex hardware was used. The method reported was fast, selective and was relatively free from interferences making it appropriate for palladium determination in different samples. Recently, a biosorption system was proposed for the preconcentration of cadmium in environmental samples [24]. In this work metallothionein isolated from rabbit liver and recombined cyanobacteria metallothionein were anchored on spherical SiO_2 particles. The biosorption behaviours of these for the sorption of Cd(II) were studied. The results obtained with recombined cyanobacteria metallothionein were better. For a range of 5-100 ng L^{-1} and sample volume of 1 mL, enrichment factor of 13.8 was observed. Other than this excellent detection limit of 1.4 ng L^{-1} was achieved.

III. FLOW INJECTION SYSTEM HYPHENATED TO INDUCTIVE COUPLED PLASMA TECHNIQUES

In Inductive coupled plasma gas plasma provides a very high temperature excitation source for atomic spectrometry. The Inductive coupled plasma (ICP) spectrometer are similar to FAAS system in its sample introduction system. The optimum uptake rate of ICP is less than FAAS systems. The advantage of ICP system over FAAS is its capability for multi-elemental detection. Inductively couples plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) are most frequently used for multielemental detection. In both ICP-OES and ICP-MS, the sample is first nebulised to an aerosol and then it is atomised and ionised in plasma. ICP-OES distinguishes between different elements by the specific light emission which is induces as a result of the excitation of atom ions in the plasma while a mass spectrometer is used in ICP-MS for separation of ions of different elements. When combined to FI ICP becomes a more versatile technique. This combination of FI-ICP minimizes time of analysis and labour and lowers risk of contamination. In 2012, a review was published on the recent advancements in the area of on-line solid-phase pre-concentration for inductively-coupled plasma techniques for the determination of mineral elements [25]. This review has discussed the advantages of the hyphenated SPE system over singular system in terms of selectivity, sensitivity, sampling frequency etc.

3.1 FI-ICP-MS

ICP-MS is a great analytical technique which is capable of providing simultaneous multielement/isotope analysis with good sensitivity. Still, the direct determination of trace metal ions in different forms in aqueous system is difficult. To overcome this, a preconcentration step is required which can be done by coupling it with a FI system [26]. In 2011, an FI-ICP-MS system was proposed for the speciation of heavy metal ions in fresh water samples [27]. A fully automated approach was suggested for discrimination in dissolved labile and stable metal-complex ions. Better detection limits in the range of from 0.005 to 0.186 μg L^{-1} were observed. The method was found to be promising for the online determination of metal-organic complexes in fresh water samples. In another automated FI-ICP-MS system based on solid phase extraction was suggested for the preconcentration of metal ions in sea-water and other water samples [28]. This method was based on the sorption of analytes onto a minicolumn filled with a chelating resin, 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass which was placed in the injection valve of FI manifold. The method reported was fast, automatic and showed good sensitivity. In other method for speciation of Sb(III) and Sb(V) in seawater by FI-ICP-MS was reported [29]. Here, a chelating resin [1,5-bis(2-pyridyl)-3-sulfophenyl methylene] thio carbonohydrazide immobilised on amino propyl-controlled pore glass (550 Å, PSTH-cpg) and an anion exchanger (Amberlite IRA-910) were used for the speciation of the two species. The proposed method was free of complex treatment procedures with organic solvents which can change the concentration of antimony species. No contamination of analytes took place as entire system was closed.

3.2 Fi-Icp-Aes/Oes

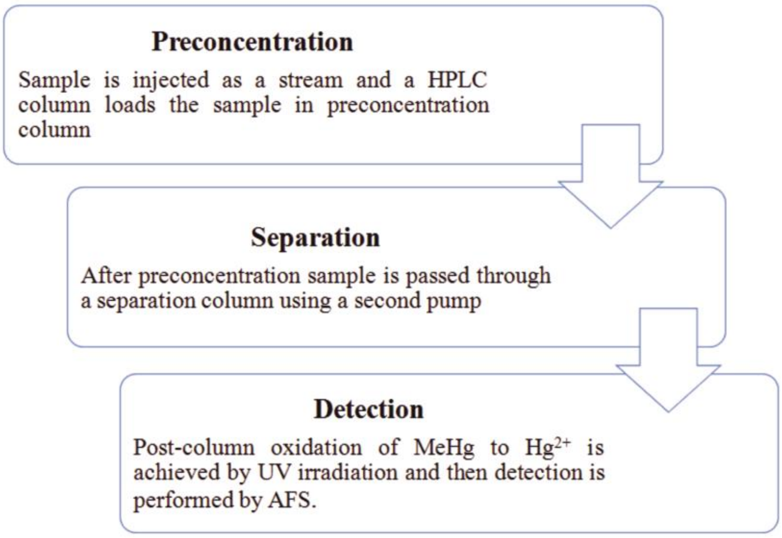
A solid phase extraction system was proposed for the determination of zinc in natural water using FI-ICP-OES. This paper has discussed the importance of FI preconcentration system in terms of low consumption of samples and reagents, high analytical throughput and minimal waste production [30]. The use of solid phase extractant for preconcentration of analyte is also highlighted. In another system SPE based fractionation method using FI-ICP-AES system was proposed for speciation of metal ions in aqueous samples [31]. The use of FI system has provided preconcentration of different species resulting in increase in sensitivity thus improving the detection limits. The coupling of FI-ICP-AES system has improved the detection limits drastically in comparison to conventional ICP-AES system. The automated control of FI system has also lowered the risk of contamination resulting in good reproducibility of results. Another advantage discussed here is as the whole process of separation and preconcentration is taking place in single step the sample throughput is also improved. Carbon nanotubes (CNTs) in a FI preconcentration system along with ICP-AES have also been used for heavy metal detection [32]. The sorption behaviour of CNTs was compared for Cd(II) preconcentration. To enhance the efficiency of system the authors have used ultrasonic nebulisation (USN). In some FI systems CNTs generate high back pressure. This can be solved by using non-compacted minicolumns. The coupling with FI has made the system fast, increased sample throughput and enhanced systems analytical performance.

IV. FLOW INJECTION SYSTEM HYPHENATED TO UV-VISIBLE SPECTROPHOTOMETRIC TECHNIQUE

In UV-Visible absorbance depends on both light absorption and diffraction. It varies with the wavelength of light and size of the particles. In organic molecules it depends on the composition of the chromophore [33]. UV-Visible spectrophotometers are most frequently coupled with FI system as a detector. To hyphenate UV-Vis with FI the intensity the cuvette is substituted with a flow through cell [6]. A novel procedure for cadmium determination was proposed [34]. This system was based on the complex formation between Cd(II), iodide ions, and 2-[2-(4-dimethylamino-phenyl)-vinyl]-1-ethyl-quinolinium iodide (R), commonly known as Quinaldine red. The reported method was quick and precise and can be applied to real samples with complex matrices. The advantages of the proposed system were that no preconcentration step such as solvent or solid phase extraction was required and no surfactant was added for solubilisation. The consumptions of reagents were less and more reproducible results were achieved with the FI system. In another recently developed system a dispersive liquid-liquid microextraction procedure was proposed for determination of copper in environmental water samples [35]. The concentration of copper in water sample is low so a preconcentration step was required. Other than the development of the preconcentration procedure, focus was drawn on the automation of the system. The hyphenation with FI system was done to make the process automated. By introducing FI technique solutions can be injected as well as re-directed and use of columns can introduce selectivity too. The entire system is computer controlled from solution injection to transport step so this increases the reproducibility of the analytical system. The developed system was based on the complex formation between copper and bathocuprine. The suggested system was fast and sensitive in terms of sensitivity, reagent consumption and linear range.

V. FLOW INJECTION SYSTEM HYPHENATED TO ATOMIC FLOURESCENCE SPECTROMETRIC TECHNIQUE

Cold vapour generation atomic fluorescence spectrometric (CVGSFS) technique is mostly used for the determination of mercury speciation in various samples. It's a selective, low cost and a very sensitive technique for the determination of mercury. Before entering in the cold vapour stage the organomercury is converted to Hg(II) by using an oxidation system. This system is a new green aspect as it avoids use of carcinogenic chemicals for mercury digestion [36]. In 2015, an analytical system was described for the speciation of mercury at ppq (pg L^{-1}) level [37]. The system was very sensitive and selective for mercury determination in water samples. Other advantages of the reported method were that it was matrix independent, cost effective, automated and high preconcentration factor was achieved. A schematic representation of FI-HPLC-CVGAFS system is given in Fig. 4. In another system, a novel analytical method was proposed using hyphenation of FI system with AFS for the speciation of mercury at ultratrace level [38]. The method was reliable, cost-effective and green. This system has photochemical vapour generation which provides system more stability and enhances the analytical characteristics as it is free from interferences. Here, mercury was first reacted with diethyldithiocarbamate forming a hydrophobic compound which is then preconcentrated using FI system. Then it was in situ converted into cold vapour using UV irradiation and then these cold vapors are passed to AFS for detection. This method can be applied for the speciation of Hg^{2+} and $MeHg^{+}$ respectively.



Sample is injected as a stream and a HPLC column loads the sample in preconcentration column

After preconcentration sample is passed through a separation column using a second pump

Post-column oxidation of MeHg to Hg^{2+} is achieved by UV irradiation and then detection is performed by AFS.

Fig. 4 A Schematic Representation of FI-HPLC-CVGAFS System.

VI. CONCLUSION

The determination of heavy metal ions in environmental samples is a crucial task. The toxic nature of these species poses a threat for both mammals and environment. The need of a sensitive and selective analytical method thus has become demand of time and nature. Few of the oxidation states of many elements are essential to us as well thus, a technique with the property of speciation will be extremely important. Many singular techniques have found application in the trace analysis of metal ions. However the increase in interferences arising from matrix ions or extremely low concentration of analyte makes the direct determination of these ions a challenging task. The hyphenation with FI system has proven to solve these issues and has made these techniques extremely selective and sensitive. The sensitivity of these techniques has reached the level of ppq (pg L^{-1}) as a result of coupling to FI system. In Table 1 a comparison of detection limits between singular and hyphenated techniques is given. As it can be clearly seen that the detection limit improves significantly after coupling the singular analytical system with FI system. Not just the sensitivity is enhanced but the system has also become automated, computer controlled program makes it even more efficient and less vulnerable to errors as well. The green aspect can also be introduced as it lowers the consumption of reagents. Thus, the hyphenation of analytical techniques to FI system has become one of the most important systems in ultratrace analysis of metal ions in various matrices.

Table 1 Comparison of Detection Limits of Singular and Hyphenated Techniques for Various Metal Determination

Detection technique	**Metal ion**	**Detection Limit ($\mu g\ L^{-1}$)**		**References**
		Singular technique	**Hyphenated technique**	
FAAS	Cr	60	0.13	14
GFAAS	Pd	50	2	23
ICP-MS	Cd	0.07	0.004	28
ICP-OES	Zn	0.1	0.08	31
AFS	Hg	0.003	4×10^{-5}	37

VII. ACKNOWLEDGEMENTS

The authors are thankful to Department of Science and Technology (DST) and University Grants Commission (UGC), New Delhi, India for financial support.

REFERENCES

[1] M. Jaishankar, T.Tseten, N. Anbalagan, B.B. Mathew and K.N. Beeregowda, Toxicity, mechanism and health effects of some heavy metals, Interdisciplinary Toxicology, 7(2), 2014, 60–72.

[2] P. C. Nagajyoti, K. D. Lee and T. V. M. Sreekanth, Heavy metals, occurrence and toxicity for plants: a review, Environment Chemistry Letters, 8, 2010, 199–216.

[3] World Health Organisation, Guidelines for Drinking-water Quality, 4th edn, 2011.

[4] J.D. Butcher, Advances in electrothermal atomization atomic absorption spectrometry: Instrumentation, methods, and applications, Applied Spectroscopy Reviews, 4, 2006, 15–34.

[5] B. Hu, S. Li, G. Xiang, M. He, and Z. Jiang, Recent progress in electrothermal vaporization–inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry, Applied Spectroscopy Reviews, 42, 2007, 203–234.

[6] Z. L. Fang, Flow Injection Atomic Absorption Spectrometry (John Wiley & Sons: Chichester, UK, 1995).

[7] X. Wen, Q.Yang, Z. Yan and Q. Deng, Determination of cadmium and copper in water and food samples by dispersive liquid–liquid microextraction combined with UV–vis spectrophotometry, Microchemical Journal, 97(2), 2011, 249–254.

[8] P. Phalke and S. Kavade, Review on Hyphenated Techniques, International Journal of Chemical Studies, 1(3), 2013, 157-165.

[9] T-L. Denga, Y-W. Chenb and N. Belzileb, Antimony speciation at ultra trace levels using hydride generation atomic fluorescence spectrometry and 8-hydroxyquinoline as an efficient masking agent, Analytica Chimica Acta, 432(2), 2001, 293–302

[10] Ruzicka, J., and E. H. Hansen. 1975. Flow injection analyses 1. New concept of fast continuous-flow analysis, Analytica Chimica Acta, 78(1), 1975, 145–157.

[11] Z. Fang, Flow Injection Separation and Preconcentration (VCH Publishers, Inc., New York, 1973).

[12] R. Saxena and S. Saxena, Flow injection preconcentration system using a new functionalized resin for determination of cadmium (II) by flame atomic absorption spectroscopy, Indian Journal of Chemistry, 51A, 2012, 1567-1573.

[13] R. Saxena, P. L. Meena and S.Tiwari, Determination of Copper in Industrial Water by Innovative Flow Injection Flame Atomic Absorption Spectrometry, Instrumentation Science and Technology, DOI: 10.1080/10739149.2015.1089275.

[14] R. Saxena, S. Tiwari and N. Sharma, Flow-injection solid phase extraction using Dowex Optipore L493 loaded with dithizone for preconcentration of chromium species from industrial waters and determination by FAAS, RSC Advances, 5, 2015, 69196–69204.

[15] R. Saxena and P.L. Meena, Flow injection online solid phase extraction system using Amberlite XAD-16 functionalized with 8-hydroxyquinoline for copper and zinc determination by flame atomic absorption spectrometry, RSC Advances, 4, 2014, 20216-20225.

[16] T .Çetina, Ş. Tokalıoğlua, A. Ülgena, S. Şahana, İ. Özentürk and C. Soykan, Synthesis/characterization of a new chelating resin and on-line solid phase extraction for the determination of Ag(I) and Pd(II) from

water, cream, anode slime and converter samples by flow injection flame atomic absorption spectrometry, Talanta, 105, 2013, 340–346.

[17] T. Daşbaşı, Ş. Saçmacı, S. Şahan, A. Ülgen and Ş. Kartal, An on-line separation and preconcentration system coupled with flame atomic absorption spectrometry for the determination of lead, Analytical Methods, 5, 2013, 3307-3313.

[18] S-Y. Zhou, N. Song, S-X. Liu, D-X. Chen, Q. Jia and Y-W. Yang, Separation and preconcentration of gold and palladium ions with a carboxylated pillar [5] arene derived sorbent prior to their determination by flow injection FAAS, Microchimica Acta, 181, 2014, 1551-1556.

[19] J.Waluvanaruk, W. Aeungmaitrepirom, T. Tuntulani and P.Ngamukot, Preconcentration and Determination of Trace Silver Ion Using Benzothiazole Calix[4]arene Modified Silica by Flow Injection Flame Atomic Absorption Spectrometry, Analytical Sciences, 30(3) , 2014, 389-395.

[20] A. M.H. Shabani, S. Dadfarnia and Z. Dehghani, On-line solid phase extraction system using 1, 10-phenanthroline immobilized on surfactant coated alumina for the flame atomic absorption spectrometric determination of copper and cadmium, Talanta, 79(4), 2009, 1066–1070.

[21] S. Dadfarnia, A.M.H. Shabani, E. Kazemi, S. A. H. Khormizi and F. Tammadon, Synthesis of Nano-Pore Size Ag(I)-Imprinted Polymer for the Extraction and Preconcentration of Silver Ions Followed by Its Determination with Flame Atomic Absorption Spectrometry and Spectrophotometry Using Localized Surface Plasmon Resonance Peak of Silver Nanoparticles, Journal of Brazilian Chemical Society, 26(6), 2015, 1180-1190.

[22] Y-H. Zhang, M. Wang, X-G. Su, T. Zheng, H-Q Zhang and Q-H. Jin, Flow Injection Semi-online Preconcentration Graphite Furnace Atomic Absorption Spectrometry for Determination of Cadmium, Copper and Manganese, Chemical Research in Chinese Universities, 18(1), 2002, 1-7.

[23] C. B. Ojeda, F.S. Rojas, and J. M.C. Pavòn On-line preconcentration of palladium(II) using a microcolumn packed with a chelating resin, and its subsequent determination by graphite furnace atomic absorption spectrometry, Microchimica Acta, 158, 2007, 103–110.

[24] T. Yang, L-Y. Ma, M-Li. Chen and J-H. Wang, Metallothionein isoforms for selective biosorption and preconcentration of cadmium at ultra-trace levels, Journal of Analytical Atomic Spectrometry, 30, 2015, 929-935.

[25] D. Das, M. Dutta, M. L. Cervera and M. de la Guardia, Recent advances in on-line solid-phase pre-concentration for inductively-coupled plasma techniques for determination of mineral elements, Trends in Analytical Chemistry, 33, 2012 35-45.

[26] J.A. Caruso, B. Klaue, B. Michalke and D.M. Rocke, Group assessment: elemental speciation, Ecotoxicology and Environmental Safety, 56, 2003, 32–44.

[27] T-T. Shih, W-Yu.Tseng, K-H. Tsai, W-Yu. Chen, M-W. Tsai and Y-C. Sun, Online coupling of ultraviolet titanium dioxide film reactor with poly(methyl methacrylate) solid phase extraction–inductively coupled plasma mass spectrometry for speciation of trace heavy metals in freshwater, Microchemical Journal, 99, 2011, 260–266.

[28] I. S.Trujillo, Elisa V. Alonso, A. G. de Torres and J. M.C. Pavón, Development of a solid phase extraction method for the multielement determination of trace metals in natural waters including sea-water by FI-ICP-MS, Microchemical Journal, 101, 2012, 87–94.

[29] A. C. Fornieles, A. G. de Torres, E. V. Alonso, M. T. S. Cordero and J. M. C. Pavón, Speciation of antimony(III) and antimony(V) in seawater by flow injection solid phase extraction coupled with online hydride generation inductively coupled plasma mass spectrometry, Journal of Analytical Atomic Spectrometry, 26, 2011, 1619-1626.

[30] L. A. Escudero , L. D. Martinez, J. A. Salonia and J. A. Gasquez, Determination of Zn(II) in natural waters by ICP-OES with on-line preconcentration using a simple solid phase extraction system, Microchemical Journal, 95, 2010, 164–168.

[31] C. Puls and A. Limbeck, Determination of trace metal fractionation in aqueous solutions using a solid phase extraction flow injection system on-line coupled to ICP-AES, Journal of Analytical Atomic Spectrometry, 24, 2009, 1434–1440.

[32] B. P. M. Savio , L. D. Martinez, R. A. Gil and P. Smichowski, Study of carbon nanotubes and functionalized-carbon nanotubes as substrates for flow injection solid phase extraction associated to inductively coupled plasma with ultrasonic nebulisation Application to Cd monitoring in solid environmental samples, Microchemical Journal, 98 , 2011, 225–230.

[33] M. Baalousha, B. Stolpe and J.R. Lead, Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: A critical review, Journal of Chromatography A, 1218 , 2011, 4078– 4103.

[34] J. Škrlíková, V. Andruch, H. Sklenářová, P. Solich, I. S. Balogh, and F. Billes, A novel non-extractive sequential injection procedure for determination of cadmium, Analytical Letters, 44, 2011, 431–445.

[35] B. Horstkotte, M. Alexović, F. Maya, C. M. Duarte, V. Andruch and V. Cerdá, Automatic determination of copper by in-syringe dispersive liquid–liquid microextraction of its bathocuproine-complex using long path-length spectrophotometric detection, Talanta, 99, 2012, 349-356.

[36] V. Angeli, S. Biagi, S. Ghimenti, M. Onor, A. D'Ulivo and E. Bramanti, Flow injection-chemical vapor generation atomic fluorescence spectrometry hyphenated system for organic mercury determination: A step forward, Spectrochimica Acta Part B, 66, 2011, 799–804.

[37] C-C. Brombach, B. Chen, W.T. Corns, J. Feldmann and E. M. Krupp, Methylmercury in water samples at the pg/L level by online preconcentration liquid chromatography cold vapor-atomic fluorescence spectrometry, Spectrochimica Acta Part B, 105, 2015, 103–108.

[38] Y. Gao, W. Yang, C. Zheng, X. Hou and L.Wu, On-line preconcentration and in situ photochemical vapor generation in coiled reactor for speciation analysis of mercury and methylmercury by atomic fluorescence spectrometry, Journal of Analytical Atomic Spectrometry, 26, 2011, 126-132.