



Chapter-VI

Summary

This thesis deals with studies relating to the development of solid-phase extraction methods for preconcentration/separation of metals Cu, Mn, Zn, Pb, Cd, Ni, Co and Fe in environmental and biological samples using Amberlite XAD resins functionalized with new dithiocarbamate and thiosemicarbazide derivatives namely with Potassium 2-benzoylhydrazinecarbodithioate (PBHCD), 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPTT) and 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT) and determination by ICP-AES.

Instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), electroanalytical techniques and X-ray fluorescence spectrometry are commonly used for the determination of metals. Compared with other techniques, ICP-AES plays a significant role in the multi-elemental analysis. But direct analysis of trace metals in environmental and biological samples by ICP-AES is a problem because of very low concentrations of these metal ions and high amounts of matrices in the analyzing samples. Therefore, the analyte must be separated from sample by removing the matrix from the sample solutions and preconcentrated before determination by ICP-AES. For this purpose, several separation and preconcentration procedures have been developed for trace metal ion determination in various matrices. These methods include liquid-liquid extraction, ion exchange techniques, coprecipitation, cloud point extraction and solid phase extraction etc. Solid phase extraction (SPE) is a well-established sample pretreatment technique in biomedical and environmental field, compared with traditional liquid-liquid extraction method. SPE has the following advantages: (i) high preconcentration factor; (ii) simple operation; (iii) rapid phase separation; (iv) can be combined with different detection techniques and (v) time saving and cost saving. SPE method involves functionalisation of solid inert support like amberlite XAD resins with good organic ligands that can selectively enrich the metal ions by forming complexes. Hence, there is a continued interest in the development of functionalized resins that can provide good stability, high sorption capacity for metal ions, and good flexibility in working conditions. In view of this we have synthesized three new organic ligands namely Potassium 2-benzoylhydrazinecarbodithioate (PBHCD), 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPTT) and 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT), which are suitable for functionalisation of Amberlite XAD-

16/XAD-2 through azo spacer (-N=N-). The functionalized resins were used for solid phase extraction of Cu, Mn, Zn, Pb, Cd, Ni, Co and Fe metal ions from water and food samples. The optimum experimental conditions for the quantitative sorption of metal ions, effect of pH, sample volume, flow rate, concentration of eluent, sorption capacity, kinetics of sorption, and the effect of diverse ions on the sorption of analytes have been investigated. These experiments led to the development of three new SPE methods.

In the first method, a dithiocarbamate Potassium 2-benzoylhydrazine-carbodithioate (PBHCD) has been synthesized and used for functionalization of Amberlite XAD-16 and the functionalized resin was used for the separation and preconcentration of metal ions, Cu(II), Mn(II) and Zn(II) in water and leafy vegetables and determined by ICP-AES. A glass column was loaded with functionalized resin and samples containing metal ions were passed through the column. After preconcentration of metal ions on column the sorbed metals were eluted with 2.0 M HNO₃ solution and determined by ICP-AES. The optimum experimental conditions for the quantitative sorption of three metals were found to be pH of 5.0 with an adsorbent dose of 400 mg and eluent of 10 mL of 2.0 M HNO₃. The accuracy of the procedure was ascertained by determining metals in standard reference material (NIST 1643e water). The developed method was applied for determination of metals in bore well water, river water, sea water and leafy vegetables. The leafy vegetable samples (Cabbage (*Brassica oleracea* var capitata), Thotakura (*Amaranthus tricolor*), Palakura (*I. frutescens*) and Chukkaku (*R. vesicarius*)) were prepared by microwave digestion and preconcentrated by SPE and determination by ICP-AES. The detection limits with this method were 5.6, 4.5 and 1.8 µg L⁻¹ for Cu (II), Mn (II) and Zn (II), respectively.

In the second method, a thiosemicarbazide derivative (Triazole), 3-(2-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT) has been synthesized and used for functionalization of Amberlite XAD-2 and the functionalized resin was used for the separation and preconcentration of metal ions, Pb(II), Ni(II), Cu(II) and Cd(II) in water and vegetables samples and determined by ICP-AES. A glass column was loaded with functionalized resin and samples containing metal ions were passed through the column. After preconcentration of metal ions on column the sorbed metals were eluted with 1.0 M HNO₃ solution and determined by ICP-AES. The optimum experimental conditions for the quantitative sorption of four metals were found to be pH of 6.0 with an

adsorbent dose of 500mg of functionalized resin and eluent of 10 mL of 1.0 M HNO₃. The accuracy of the procedure was ascertained by determining metals in standard reference material (NIST 1643e water). The developed method was applied for determination of metals in river water, sea water and food samples. The vegetable samples like Lady's Finger (*Abelmoschus esculentus*), Onion (*Allium sepa*), Cucumber (*Cucumis sativus*), Tomato (*Lycopersicum esculentum*) and Drumstick (*Moringa oleifera*) were prepared by micro wave digestion and preconcentrated by SPE and determination by ICP-AES. The detection limits with this method were 0.16, 0.20, 0.18 and 0.22 $\mu\text{g L}^{-1}$ for Pb(II), Ni(II), Cu(II) and Cd(II) respectively.

In the third method, a thiosemicarbazide derivative (Triazole), 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT) has been synthesized and used for functionalization of Amberlite XAD-16 and the functionalized resin was used for the separation and preconcentration of metal ions, Cu(II), Fe(II), Co(II) and Mn(II) in water and vegetables samples and determined by ICP-AES. The optimum experimental conditions for the quantitative sorption of four metals were found to be pH of 5.0 with an adsorbent dose of 500 mg and eluent of 10 mL of 1.0 M HNO₃. The accuracy of the procedure was ascertained by determining metals in standard reference material (NIST 1643e water). The developed method was applied for determination of metals in tap water, river water and vegetable samples. The vegetable samples like Cauliflower (*Brassica olera. var. Botrytis*) and Sweet Potato (*Ipomoea*) were prepared by micro wave digestion and preconcentrated by SPE and determination by ICP-AES. The detection limits with this method were found to be 0.9, 0.4, 0.7 and 0.8 $\mu\text{g L}^{-1}$ for Co(II), Cu(II), Mn(II) and Fe(II) respectively.

The result showed that the solid-phase extraction methods developed based on Amberlite XAD-16 resin functionalised with dithiocarbamate (PBHCD) Amberlite XAD-2 resin functionalized with 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPTT) and Amberlite XAD-16 functionalized with 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione had high sorption capacities, which indicates good potential for separation and preconcentration of metals from environmental and food samples. The strong metal binding property of PBHCD, NPTT and HPTT combined with the insolubility of metal complexes in water and capacity to form chelate complexes are the reasons for high sorption capacities exhibited by the developed resins. The high

enrichment factors, fast kinetic rates, stability of modified/functionalized resins in acids and lower detection limits along with the free from interferences by the matrix constituents made the suitability of the developed solid-phase extraction methods for preconcentration of trace metals in environmental and food samples and subsequent determination by ICP-AES.