CHAPTER – VI
Solid phase extraction of Co(II), Ni(II), Mn(II) and Cr(III) using 6-aminopyridin-2-yliminomethylnapthalen-2-ol (APIMN) modified SiO$_2$ nanoparticles prior to determination by FAAS

6.1 INTRODUCTION

Transition metals have been used in many different areas for thousands of years. However, heavy transition metal ions are toxic, non-biodegradable and tend to be accumulated in the human vital organs, where they can act progressively over a long period through food chains. The monitoring of trace heavy metal ions in environmental samples have received increasing attention \cite{1-3}. However, due to the complexity of sample matrix and the frequently low concentrations of metals, there is a crucial need for the extraction and preconcentration of trace elements from matrix before their analysis using atomic absorption spectrometry or other techniques. To obviate these problems, an effective extraction and preconcentration method is necessary. In the last two decades, the solid phase extraction (SPE) approach has gained rapid acceptance. It is considered as alternative to the classical liquid extraction technique, owing to several major advantages in application such as fast, simple, amenability to automation, low disposal costs and extraction time for sample preparation \cite{4,5}. Various functional groups are immobilized onto a solid support matrix as a solid phase extractant for the purpose of extraction and enrichment of trace metal ions from environmental samples. Silica gel as a solid support is of great importance because it possesses some definite advantages \cite{6}, such as non deforming, good mechanical strength and heat-stable. In addition, chelating agents can be easily loaded onto the silica gel with high stability, or be bonded chemically to the support, that affording a higher stability \cite{5}.

Recently, some chelating agents have been modified on the silica gel as solid phase extractants for the preconcentration of some metal ions. Salicylaldoxime \cite{6}, 8-hydroxy quinoline \cite{7}, 1-(2-thiazolylazo)-2-naphthol \cite{8}, dithizone \cite{9}, acid red-88 \cite{10}, N-(3-propyl)-O-phenylenediamine \cite{11}, thiophene-2-carbaldehyde \cite{12}, aminothioamidoanthraquinone \cite{13}, formylsalicylicacid \cite{14}, thiourea \cite{15}, 2-mercaptobenzothiazole \cite{16}, dithiocarbamate \cite{17}, iminosalicyl- \cite{18}, o-vanillin \cite{19}, 2-hydroxy-5-nonylacetopheneoxime \cite{20}, glycerol \cite{21},
2-thiophene carboxaldehyde, 1,5-diphenylcarbazide, 1,5-bis(di-2-pyridyl) methylene tiocarbohydrazid, 2,4,6-trimorpholino-1,3,5-triazin, 1,3-diamine propane-3-propyl, 3-(1-imidazolyl)propyl, thioacetamide, methylthiosalicylate are reported as the chelating matrix for various metal ions. The magnetic core of MNPs (Magnetic Nano Particle) is mainly iron, nickel, cobalt, and their oxides. Most often these include iron oxides, such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃). However, pure iron oxides are prone to aggregate, resulting in loss of their magnetism. The most commonly used material for coating the core of MNPs is silica, which carries various functional groups. The extensive use of silica is primarily due to the general availability of the material, but also its specific properties. The silica can be applied to the magnetic core as a result of the sol-gel process. The application of the Stöber method allows control of the size, the porosity and the morphology of the MNPs. Materials obtained by this method are spherical and uniformly dispersed. MNPs are available in a wide range of sizes – from NPs to microparticles. However, typically NPs with a diameter of 1–100 nm are used.

Among the methods for preparing the magnetic core of MNPs, we can mention co-precipitation, hydrothermal synthesis, thermal decomposition, colloidal and high-energy ball mill. The co-precipitation method was used throughout an experiment to obtain magnetite MNPs. Previous studies have shown the excellent photocatalytic activity of some ferrite nanoparticles. Many studies have been devoted to the examination of organic compound photo degradation in the presence of H₂O₂ and TiO₂. To date, many methods have been developed to synthesize spinel ferrite nanoparticles, such as aerosol route, co-precipitation method, ceramic technique, hydrolysis method, microwave-hydrothermal method, and hydrothermal method. The hydrothermal process has been widely used to synthesize the spinel ferrites because of its simple process, low cost, low synthesis temperature and small particle size. But most of these immobilized ligands cannot provide strong coordination sites with many metal ions. Anchoring a multidentate ligand on the surface of silica gel may further enhance the chelating ability of solid phase matrix.

Water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Moreover, water pollution is considered to be a major environmental problem worldwide, and among the various water pollutants, heavy metals require special attention because of their toxic effect on humans and the environment. Heavy metals are considered to be the most important pollutant in source and treated water. The increased use of heavy metals industrially resulted in an increase in...
the availability of metallic substances in natural source water. Moreover, heavy metals form a very dangerous category due to their toxic and carcinogenic nature, non-biodegradable and hence, tend to accumulate in the environment for long time. Some of these toxic elements are cadmium, lead, mercury, nickel, chromium and zinc. Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatments. Several studies have addressed nanoparticles, mainly metal oxides, as effective and efficient adsorbents in the cleanup of environmental contaminants, mainly because nanoparticles can penetrate into the contamination zone where microparticles cannot.

Conventional techniques for removing heavy metals from water and wastewater include electroplating, evaporating, membrane filtration, oxidation, reduction, ion exchange and adsorption. Among these methods, adsorption is the most effective technique. Various adsorbents such as activated carbon, silica gel, and graphite oxide can be used in the purification of water. Historically, graphite oxide and other carbon based nanomaterials have been used as adsorbent for environmental purification and water treatment applications for the removal of inorganic and organic pollutants.

Contamination of the environment by heavy metals has attracted growing concern due to the health risks they pose for humans and animals. The Pb(II) ion is regarded as the pollutant that requires priority control due to its ability to bioaccumulate in the food chain. The Cr(III) ion has been commonly found in effluents from industries such as mining, leather tanning, chrome plating, and textiles. It has the ability to bind proteins and nucleic acids which can damage ecological systems. To date, conventional techniques for removing heavy metal ions include precipitation, adsorption, ion exchange, membrane filtration, electrochemical treatments, coagulation, reverse osmosis, and biosorption processes. However, most of these strategies are costly and suffer from drawbacks like the disposal of metal-bearing sludge and secondary wastes. As one approach, adsorption has been employed as an effective and economical method for removing metal ions from wastewater.

Various adsorbents including activated carbons, natural and synthetic polymers, nanosized metal oxides, clay minerals, zeolites, and biomasses have been utilized. Of this range of materials, magnetite nanoparticles exhibit a promising potential due to its combination of nanoparticle properties, specifically the large ratio of surface-to-volume, highly active sites and magnetic properties. These features make it easy to separate metal
loaded magnetic adsorbent from a solution for further recycling or regeneration. Using magnetite nanoparticles to remediate metal ions in wastewater is one of the new approaches. To date, most of the adsorption using magnetite concerns the removal of a single metal ion rather than the removal of mixed heavy metals though recently the adsorption of Cu(II) and Cr(VI) using amino-functionalized nano-Fe₃O₄ magnetic polymers have been reported. Nevertheless, further studies to identify the competitive effects of mixed contaminants on Fe₃O₄ nanoparticles are necessary to understand the co-adsorption since industrial wastewaters often contain mixed metal ions. In addition, despite increasing research efforts to gauge the removal efficiency of nanosized Fe₃O₄, the co-adsorption mechanism is still unknown. Nonetheless, understanding the removal mechanism of bare Fe₃O₄ is integral for designing effective wastewater treatment materials since nano-Fe₃O₄ is commonly used as the magnetic core for composite sorbents in the remediation of heavy metal ions. Finally, our previous studies showed Cr(VI) was partially reduced to trivalent chromium [Cr(III)] using nZVI, which was then oxidized to form iron oxides after reaction.

APIMN is a good ligand with high affinity to metal ions and it was also thought worthwhile to be immobilized on the surface of silica gel after grafting and may fulfil the objective of high chelating ability. The present work aims to synthesize a APIMN functionalized silica nanoparticle as chelating matrix. It is used as a solid phase extractant for extraction and preconcentration of Co(II), Ni(II), Mn(II) and Cr(III) from environmental samples. The 6-aminopyridin-2-yliminomethylnapthalen-2-ol (APIMN) modified with SiO₂ solid phase extractant has been developed for the preconcentration of Co(II), Ni(II), Mn(II) and Cr(III) in environmental samples. The novel prepared solid phase extractant is characterized by the Fourier transform infrared spectroscopy and SEM. The pH ranges for quantitative sorption and the concentrations of HNO₃ for eluting Co(II), Ni(II), Mn(II) and Cr(III) were optimized, respectively. The sorption capacity of the matrix has been found to be 10.63, 5.09, 12.38, 6.62 mg/g for Co(II), Ni(II), Mn(II) and Cr(III) respectively, with the preconcentration factor ~150. The effect of flow rates, the eluents and the electrolytes and cations on the metal ions extraction as well as the chelating matrix stability and reusability were also studied. The extraction behavior of the matrix was confirmed with Langmuir's equation. The proposed preconcentration procedure was successfully applied to the analysis of Co(II), Ni(II), Mn(II) and Cr(III) in environmental samples. The
detection limit and quantification limit for Co(II), Ni(II), Mn(II) and Cr(III) were found to be 0.48, 0.28, 0.46, 0.69 μg/L and 1.02, 1.24, 0.28, 1.16 μg/L, respectively.

**Apparatus**

Fourier transform infrared (FT-IR) absorption spectra were recorded with the Spectrum 2000 (Perkin-Elmer). A Varian Spectra AA55 atomic absorption spectrometer, equipped with air–acetylene flame was used for metal ion determination. The wavelength used for monitoring Co, Ni, Mn and Cr is 283.3, 232.0, 403.0 and 357.9 nm respectively. Scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 scanning electron microscope with an acceleration voltage of 20 kV. The pH measurements were conducted by a pH-meter (Elico Model LI-129, Hyderabad, India). A glass tube (200 mm × 10 mm i.d.) was used to study the metal ion sorption on the chelating matrix and washed with 3.0 M HCl, 3.0 M HNO₃, ethanol and deionised water successively. The flow rate of solution through the column was controlled using a peristaltic pump.

**Reagents**

Silica nanoparticle (SG) (60–100 mesh size) and APIMN were purchased from Sigma Aldrich, India. 4-(trihydroperoxysilyl) butanoic acid was procured from Across chemicals, India. Stock solutions of Co(II), Ni(II), Mn(II) and Cr(III) (1.0 mg/mL) were prepared from analytical reagent grade CoCl₂, MnSO₄·5H₂O, CrCl₂, NiSO₄·7H₂O by dissolving the appropriate amounts in deionised water, then acidified with 5 mL of concentrated nitric acid. All working solutions were diluted according to requirements. An acetate–acetic acid buffer (pH 3.0–5.0), phosphate buffer (pH 6.0–7.0), NH₃–NH₄Cl buffer (pH 8.0–10.0) were used for pH adjustment. All chemicals used were of analytical reagent grade.

**Batch experiments**

APIMN-SG (0.1 g) was equilibrated with a buffer solution containing suitable amount of metal ions in a glass stoppered bottle (250 mL) for a fixed period of time. The unextracted transition metal ion in the solution phase was measured by flame atomic absorption spectrometry (FAAS). This method was used to study the effect of shaking time on the retention of transition metal ions on present matrix and also to measure the maximum adsorption capacity, adsorption isotherms etc.
**Column experiments**

In the column experiments, APIMN-SG (1.0 g) was packed in a glass tube and a solution containing metal ions (Co(II), Ni(II), Mn(II) and Cr(III)) was adjusted to a suitable pH and percolated at a certain flow rate. The transition metal ion retained on the column was eluted with a suitable eluant and determined by FAAS.

**Sample preparation**

A certified reference material, fresh water (SRM 1643e), was obtained from the National institute of Standards and Technology (NIST), India. 0.500 g of this certified water sample was transferred to a closed polytetrafluoroethylene (PTFE) beaker. Then, 7, 4 and 4 mL of concentrated HNO₃, HClO₄ and HF were added respectively. The mixture was heated at 368 K for 12 h and evaporated nearly to dryness. After cooling, the residue was dissolved in 50 mL of 1.0 M HCl, and the solution was filtered. The tap and river water samples were obtained from Lab and Penna River (Nellore, A.P., India), and acidified with 2% HNO₃. The samples were then filtered and the filtrates were stored in glass bottles, known amount of Co(II), Ni(II), Mn(II) and Cr(III) was added to this water sample and used for analysis within 3 days.

**6.2 RESULTS AND DISCUSSION**

**Characterization of APIMN-SG**

The proposed chemical structure of the newly synthesized silica gel phase (APIMN-SG) is shown in Figure- 1. It has been characterized by FTIR spectra and elemental analysis (Figure- 2). The elemental analysis of APIMN-SG suggests that 0.336 mmol/g of functional group has been grafted onto the surface of silica gel. The FTIR spectrum of APIMN-SG exhibits a band at 1688 cm⁻¹ which appears to be contributed by C=O stretching vibration and a strong band (707 cm⁻¹) of –CH₂–NH–CH₂–bending vibration can be seen. The phenyl vibrations appear at 1618, 1501, 1430, 1318 cm⁻¹. All these observations support the grafted of APIMN on the surface of silica gel.

Figure- 3 displays the SEM image of SG and APIMN-SG, which illustrates the uniform size distribution of these nanoparticles. The diameter of nanoparticles is about 400 nm, and most of the particles are spherical in shape. As can be seen, the APIMN modified SG nanoparticles were porous microspheres and the microspheres were smooth and uniform.
Figure-1. SiO$_2$ immobilized with APIMN
Figure-2. FTIR spectrum of APIMN-SG
Figure 3. SEM images of SiO₂ and modified APIMN-SG
Effect of pH

The heavy metal ion solutions were adjusted to a desired pH (between 1.0 and 10.0) and passed through a column filled with APIMN-SG at optimum conditions. The analytes were then eluted using 10 mL HCl from the column and determined by FAAS, which gave the percentage recoveries of the eluted heavy metal ions at various pH. The effect of pH on adsorption was also studied using batch method and the results were found to be consistent with those of column method. The retention experiments were carried out in triplicate to determine the precision of the method. Figure- 4 shows the effect of pH on the retention of heavy metal ions on the APIMN-SG. It was found that the heavy metal ions retention on APIMN-SG is highly depend on the pH of the sample solution and cannot be quantitatively adsorption. The modified silica gel can quantitatively sorption these ions over a wide range of pH 4.0-8.0 for Co(II), Ni(II), Mn(II) and Cr(III), respectively. The adsorbed heavy metal ions are not significantly desorbed by distilled water, which indicates the chelating process contributes predominantly to the retention of these heavy metal ions. When pH > 10.0, the silica gel is prone to hydrolysis at high pH.
Figure-4. Effect of pH on adsorption of Co(II), Ni(II), Mn(II) and Cr(III)
Effect of eluent

The elution of Co(II), Ni(II), Mn(II) and Cr(III) from APIMN-SG was examined by using various eluants in the column experiment. Several solutions, such as HCl, HNO₃, H₃PO₄, EDTA and thiourea were tested. The results showed that using thiourea, EDTA and H₃PO₄ does not give reproducible results (recovery < 50%). HCl was found to be the most suitable eluant for stripping off the adsorbed heavy metal ions. At optimum conditions, the effect of concentration of stripping solution on desorption of the analyte from the column was investigated by using 10 mL volumes of various concentration of HCl (0.01–5.0 M). The results showed that the optimum concentration ranges of HCl for Co(II), Ni(II), Mn(II) and Cr(III) were 0.05–5.0 M, respectively. It was found that 10 mL of volume of eluant was sufficient to obtain the recovery of 96.70–98.90% for heavy metal ions as shown in Figure-5.
Figure-5. Effect of eluent concentration on the retention of Co(II), Ni(II), Mn(II) and Cr(III)
Effect of flow rate

The degree of metal ion adsorbed on APIMN-SG was studied at various flow rates (1.0–5.0 mL/min). The optimum flow rate for Co(II), Ni(II), Mn(II) and Cr(III) are shown in Figure-6. However, there was a decrease in the percentage of extraction for Co(II), Ni(II), Mn(II) and Cr(III) at flow rate higher than 2.5 mL/min respectively, because of the heavy metal ions cannot be adsorbed sufficiently by the modified silica gel (APIMN-SG). Therefore, the flow rate was maintained at 2.5 mL/min throughout the column experiment. For desorption, these metal ions can be desorbed quantitatively by the present matrix at a flow rate of 2.5 mL/min, the recovery for Co(II), Ni(II), Mn(II) and Cr(III) was <98%. 
Figure 6. Effect of flow rate on the recoveries
Adsorption isotherm

The adsorption isotherms were determined using the batch experiments at room temperature. Solutions of heavy metal ions over the concentration range of 20–180 µg/mL were maintained at the optimum pH (pH 6.0) with 15 mL buffer and shaken for 24 h with the APIMN-SG (0.1 g). The metal ions in the supernatant were determined by FAAS and the amount of heavy metal adsorbed was calculated using Eq.(1) as follows:

\[
q = \frac{V(C_0 - C)}{m}
\]  

(1)

where \( C_0 \) is the initial concentration of heavy metal ions (in µg/mL), \( C \) the equilibrium concentration of heavy metal ions (in µg/mL), \( V \) the volume of heavy metal ion solutions, \( m \) the mass of the APIMN-SG (in g) and \( q \) is amount of heavy metal ions adsorbed per gram of modified silica gel. Adsorption isotherm is often described by the Langmuir (2) and the Freundlich (3) equations:

\[
\frac{C_{eq}}{q} = \frac{C_{eq}}{b q_m} + \frac{1}{b q_m}
\]  

(2)

Where \( b \) is a Langmuir constant. \( q_m \) a constant representing adsorption capacity, also known as monolayer coverage of the surface and is a constant related to \( b \). \( C_{eq} \) is adsorbate concentration in the solution at equilibrium.

\[
\log q = \left( \frac{1}{n} \right) \log C_{eq} + \log K_F
\]  

(3)

In Eq. (3), \( K_F \) and \( n \) are constants characteristic of the system, where \( K_F \) is a measurement of adsorption capacity and \( 1/n \) of adsorption intensity.

Langmuir and Freundlich constants were determined by using the adsorption data through batch experiment. By comparing the correlation coefficients, it can be concluded that the experimental data fit the Langmuir model \( (R^2: 0.9959, 0.9962, 0.9909, 0.9948 \text{ for Co(II), Ni(II), Mn(II) and Cr(III), respectively}) \) better than the Freundlich model \( (R^2: 0.9791, 0.9085, 0.4773, 0.8721 \text{ for Co(II), Ni(II), Mn(II) and Cr(III), respectively}) \), because in the former case all the correlation coefficients were higher than 0.990. The metal ion sorption values by APIMN-SG at optimum pH is decrease in the following order: \( \text{Ni(II)} > \text{Co(II)} > \text{Cr(III)} > \text{Mn(II)} \) indicating that the highest affinity is towards Mn(II) extraction and the lowest for Ni(II).
Total sorption capacity

The sorption capacity for Co(II), Ni(II), Mn(II) and Cr(III) was determined by shaking 0.1 g of the APIMN-SG with a 100 mL of 100 μg/mL heavy metal ion solution (total amount of metal available for adsorption is much greater than the adsorption capacity) at pH 6.0 for 24 h according to the recommended batch equilibrium procedure at room temperature. The loading capacity of the APIMN-SG for each metal ion was calculated from the different batch experiments (n = 4). The average values are 12.63 (R.S.D. = 3.34%), 6.09 (R.S.D. = 2.58%), 15.38 (R.S.D. = 1.92%), 4.62 mg/g (R.S.D. = 4.60%) for Co(II), Ni(II), Mn(II) and Cr(III), respectively.

Kinetics of metal sorption

The time taken for the extraction of the metal ions and the attainment of the equilibrium condition by the APIMN-SG is of considerable importance. APIMN-SG (0.1 g) was equilibrated by shaking with 200 mL of a solution containing 10 mg of heavy metal ion for different time intervals (2, 5, 10, 15, 20, 25, 30, 40, 50 and 60 min) and the recommended batch experiment was applied. The metal ions were four–six times in excess over the sorption capacity. The concentration of heavy metal ions in the supernatant solution was determined and the amount of heavy metal adsorbed was calculated using Eq. (1) and the amount of metal ion loaded on the APIMN-SG was calculated by mass balance (in μg/g APIMN-SG). The loading half time $t_{1/2}$, defined as the time need to reach 50% of the present matrix total loading capacity, was estimated from the curves (Figure-7). From the kinetics of Co(II), Ni(II), Mn(II) and Cr(III) uptake, it was observed that an equilibration time of about 30 min was required for 95–98% sorption. However, the loading half time $t_{1/2}$ was <5 min for Co(II), Ni(II), Mn(II) and Cr(III).
Figure-7. Kinetics of heavy metal ion sorption on APIMN-SG
Effects of electrolytes and cations

The effect of various electrolytes and cations, such as NaCl, NaNO₃, KNO₃, Na₂SO₄, Na₃PO₄, Cu(II), Pb(II), Cd(II), Hg(II), Fe(III), Ca(II) and Mg(II) on the retention of heavy metal ions was examined. For this purpose, 50 mL of the test solution containing 30 μg of the studied heavy metal ion and other ions at various concentrations was passed through the column under optimum conditions. The amount of target heavy metal ion extracted was determined after elution. The tolerance limit was taken as the maximum concentration of the foreign substances which caused an approximately ±5% relative error in the determination. The tolerance limits of these substances in enrichment of Co(II), Ni(II), Mn(II) and Cr(III) on the present matrix are given in Table-1. The results shown that the presence of solid phase matrix might be used to enrich all the four heavy metal ions from environmental water samples, as their common constituents at normal level do not adversely affect the adsorption efficiency of the matrix.
Table-1. Tolerance limit of electrolytes and cations

<table>
<thead>
<tr>
<th>Electrolytes / Cation</th>
<th>Metal ion</th>
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<tbody>
<tr>
<td></td>
<td>Co(II)</td>
<td>Ni(II)</td>
<td>Mn(II)</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.80</td>
<td>0.50</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>KNO₃</td>
<td>1.20</td>
<td>1.00</td>
<td>1.20</td>
<td>0.20</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>1.60</td>
<td>1.60</td>
<td>1.80</td>
<td>1.20</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.80</td>
<td>0.02</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>0.02</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>0.50</td>
<td>0.10</td>
<td>0.60</td>
<td>0.50</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>0.30</td>
<td>0.01</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>Cr(IV)</td>
<td>0.01</td>
<td>0.06</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.08</td>
<td>0.03</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.04</td>
<td>0.01</td>
<td>0.04</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Stability and reusability of APIMN-SG

Mn(II) was chosen to determine the stability of APIMN-SG. A 0.1 g of the present matrix was immersed in 15 mL pH 1.0–10.0 buffer solutions for 24 h and then filtered off, washed with deionized water and dried at 333 K. After this treatment, the adsorption capacity of Mn(II) was determined. The result was shown in Figure- 8. It was found that the adsorption capacity is only slightly reduced in the pH range from 1.0 to 10.0. Since the solid support tends to be hydrolysis, the adsorption capacity was not determined at high pH conditions.

Preconcentration factor, limits of detection and quantification

Solutions containing 10 μg of the studied heavy metal ion in various volumes were passed through the column packed with 1.0 g of APIMN-SG, and the target heavy metal ion preconcentrated on the column was eluted and determined by the above mentioned procedure. The feed volumes for loading are shown in Fig 9. The preconcentration factor are 150 for Co(II), Ni(II), Mn(II) and Cr(III), respectively. The limits of detection and the limits of quantification are Co(II), Ni(II), Mn(II) and Cr(III) were found to be 0.48, 0.28, 0.46, 0.69 μg/L and 1.02, 1.24, 0.28, 1.16 μg/L respectively.
Figure- 8. The stability of APIMN-SG (pH 1.0–10.0 buffer solutions).
Figure- 9. Effect of sample volume
Analytical performance

The calibration curves used to determine metal ions with FAAS were made by measuring the absorbance of the working calibration solution (without any enrichment on the present matrix) at optimum operation parameters of the instrument (viz. wavelength, slit width, lamp current, etc.) and the solution conditions (viz. the acid concentration). The linear ranges for measurement have been found to be 1.0-5.0, 0.4-2.6, 0.2-1.0 and 1.0-5.0 μg/mL for Co(II), Ni(II), Mn(II) and Cr(III) respectively. The linear equation along with regression \( R^2 \) for calibration curve of each metal ion is given in Table-2.

The fresh water reference material (SRM 1643e, India) was used for method validation. As seen in Table-3, the results were compared with the certified values using a \( t \)-test at 95% confidence limits. Good agreement was obtained between the estimated content by the proposed method and the certified values for four metal ions. These results also indicate that the proposed preconcentration method for Co(II), Ni(II), Mn(II) and Cr(III) is not affected by potential interferences from the major matrix composition of the analyzed river sediment.
Table-2. Linear regression equation and correlation coefficient for Co(II), Ni(II), Mn(II) and Cr(III) by FAAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Linear equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>$A=0.005C+0.002$</td>
<td>0.9982</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>$A=0.156C+0.005$</td>
<td>0.9996</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>$A=0.305C+0.061$</td>
<td>0.9990</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>$A=0.005C+0.006$</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

$^a$All the statistical calculations are based on the average of five reading for each standard solution in the given range  
$^b$A is the peak height absorbance and C is the concentration in $\mu$g/ml
Table 3. Determination of Co(II), Ni(II), Mn(II) and Cr(III) ions in certified reference materials

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Certified Value (µg/kg)</th>
<th>Found by present method (µg/kg)</th>
</tr>
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<tbody>
<tr>
<td>Co(II)</td>
<td>26.40±0.32</td>
<td>26.10±0.32</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>60.89±0.67</td>
<td>60.20±0.67</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>38.02±0.44</td>
<td>37.50±0.44</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>19.90±0.23</td>
<td>18.60±0.23</td>
</tr>
</tbody>
</table>

Analysis of environmental samples
At the optimum conditions, water samples (2000 mL) were passed through the column for preconcentration and determination of the target heavy metal ions directly. The data listed in Table-4, shows that the recovery of Co(II), Ni(II), Mn(II) and Cr(III) from the tap water and river water samples are satisfactory.

Based on the results shown in Table-5, the sorption capacity of APIMN-SG was better than some known solid phase extractants. The adsorbed heavy metal ions can readily be desorbed by low concentration acid. The relative short adsorption time \((t_{1/2})\) of APIMN-SG for Co(II), Ni(II), Mn(II) and Cr(III) makes the analytical procedure reasonably fast. As indicated by the results of tap and river water analysis, the matrix effect with the APIMN-SG is low. The feasibility of the repeated use of APIMN-SG is an additional advantage.
Table-4. The accuracy test results for spiked recovery (sample volume: 100 mL, n=3)

<table>
<thead>
<tr>
<th>Element Added (mg/L)</th>
<th>Found (mg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tap water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.3</td>
<td>93.0</td>
</tr>
<tr>
<td>50</td>
<td>49.7</td>
<td>99.4</td>
</tr>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.7</td>
<td>97.0</td>
</tr>
<tr>
<td>50</td>
<td>48.5</td>
<td>97.0</td>
</tr>
<tr>
<td>Mn(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.8</td>
<td>98.0</td>
</tr>
<tr>
<td>50</td>
<td>49.6</td>
<td>99.2</td>
</tr>
<tr>
<td>Cr(III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.5</td>
<td>95.0</td>
</tr>
<tr>
<td>50</td>
<td>48.9</td>
<td>97.8</td>
</tr>
<tr>
<td><strong>River water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.9</td>
<td>99.0</td>
</tr>
<tr>
<td>50</td>
<td>48.5</td>
<td>97.0</td>
</tr>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.6</td>
<td>96.0</td>
</tr>
<tr>
<td>50</td>
<td>49.3</td>
<td>98.6</td>
</tr>
<tr>
<td>Mn(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.8</td>
<td>98.0</td>
</tr>
<tr>
<td>50</td>
<td>49.9</td>
<td>99.8</td>
</tr>
<tr>
<td>Cr(III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.6</td>
<td>96.0</td>
</tr>
<tr>
<td>50</td>
<td>48.4</td>
<td>96.8</td>
</tr>
</tbody>
</table>
Table-5. Comparative data from some recent studies for preconcentration of heavy metals using column SPE methods and detection by FAAS

<table>
<thead>
<tr>
<th>System</th>
<th>Studied metals</th>
<th>pH</th>
<th>Eluent</th>
<th>Flow rate (mL min⁻¹)</th>
<th>PF</th>
<th>Resin capacity (mg g⁻¹)</th>
<th>LOD</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diaion SP-850/Alpha-benzoin oxime</td>
<td>Cr, Mn, Fe, Co, Cu, Cd, Pb, Cu, Zn</td>
<td>8.0</td>
<td>1 mol L⁻¹ HNO₃</td>
<td>5</td>
<td>50</td>
<td>2.2-6.0</td>
<td>0.28-0.78</td>
<td>75</td>
</tr>
<tr>
<td>Activated carbon/ammonium pyrrolidinedithiocarbamate</td>
<td>Cd, Cu, Ni, Zn</td>
<td>5.0</td>
<td>1 mol L⁻¹ HNO₃ in acetone</td>
<td>1.0</td>
<td></td>
<td>-</td>
<td>-</td>
<td>19-28</td>
</tr>
<tr>
<td>Amberlite XAD-2010/DDTC</td>
<td>Cu, Mn, Co, Ni, Cd, Pb</td>
<td>6.0(8.0 for Mn)</td>
<td>1 mol L⁻¹ HNO₃ in acetone</td>
<td>10.0</td>
<td>100</td>
<td>5.7-6.3</td>
<td>0.08-0.26</td>
<td>77</td>
</tr>
<tr>
<td>Amberlite XAD-4/di-2-pyridyl ketone thiosemicarbazone</td>
<td>Co, Ni, Fe, Cu</td>
<td>6.0</td>
<td>1 mol L⁻¹ HNO₃ in acetone</td>
<td>0.5</td>
<td>200</td>
<td>2.0</td>
<td>30-50</td>
<td>78</td>
</tr>
<tr>
<td>DowexOptipore V-493/dibenzyldithiocarbamate</td>
<td>Cd, Pb</td>
<td>2.0</td>
<td>1 mol L⁻¹ HNO₃ in acetone</td>
<td>4.0</td>
<td>50</td>
<td>7.3-8.6</td>
<td>0.43-0.65</td>
<td>79</td>
</tr>
<tr>
<td>Amberlite XAD-4/DDTC</td>
<td>Cd, Cu, Fe, Cu, Ni, Bi</td>
<td>6.0</td>
<td>Acetone</td>
<td>5.0</td>
<td></td>
<td>-</td>
<td>-</td>
<td>2.0-23.0</td>
</tr>
<tr>
<td>APIMN-SG</td>
<td>Co(III), Ni(II), Mn(II) and Cr(II)</td>
<td>7.0</td>
<td>HCl</td>
<td>3.0</td>
<td>150</td>
<td>2.0</td>
<td>0.28-0.69</td>
<td>Present work</td>
</tr>
</tbody>
</table>
6.3 CONCLUSIONS

In this work, APIMN-SG was synthesized and a novel method of APIMN-SG-FAAS has been developed for the determination of trace amounts of Co(III), Ni(II), Mn(II) and Cr(II) in environmental samples. The prepared adsorbent, with a large surface area, could be separated from the matrix solution easily due to the APIMN-SG. The prepared APIMN-SG were characterized with SEM and FT-IR. Compared with the conventional methods, the developed method provided high enrichment factor and low LODs. It was suitable for the determination of Co(II), Ni(II), Mn(II) and Cr(III) elements in environmental samples with large volume and complex matrix.
6.4 REFERENCES


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