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Chelating Resin Based on Silica Gel for Solid-Phase Extraction Coupled with Flame Atomic Absorption Spectrometric Determination of Nickel and Cadmium

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Chelating resins offer a fast, accurate and simple method for separation and preconcentration of metal ions at low concentrations prior to their determination by an instrumental method. Silica gel-based chelating resin with chemically immobilized aurintricarboxylic acid was synthesized, characterized and used to determine Ni(II) and Cd(II) at trace levels, coupled with their analysis by flame atomic absorption spectrometer. The resin had sorption capacities of 0.21 mmol g^{-1} and 0.10 mmol g^{-1} for Ni(II) and Cd(II), respectively. The analytical detection limit (N = 20) was 1.70 μg L^{-1} for Ni(II) and 1.90 μg L^{-1} for Cd(II). The proposed method was useful for the quantitative determination of Ni(II) and Cd(II) in some commercial and water samples.

Keywords: Flame atomic absorption spectrometry, Separation, Preconcentration, Chelating resin, Aurintricarboxylic acid, Silica gel.

INTRODUCTION

Trace analysis of metal ions poses a challenge to most analytical chemists. This is mainly due to two reasons. Firstly, the metal ions, present at very low concentration levels, may not be detected by the instrumental methods. Secondly, these metal ions are usually associated with some matrix components, which causes an error in the determination of metal ions. This calls for an effective method for the metal ion concentration before analysis and separation of metal ions from the matrix components to reduce the errors caused prior to their determination by instrumental methods [1].

Methods developed for separation and preconcentration of trace metal ions [2] include precipitation [3,4], solvent-solvent micro-extraction methods [5-7], electrocoagulation [8,9], photocatalysis [10], ultrafiltration [11,12] and sorption of metal ions using chelating resins [13]. The use of chelating resins for separation and preconcentration of metal ions is widely used as this method is generally simple, easy to design, does not require any sophisticated instrumentation and economical. The same chelating resin may be used multiple times and, is generally a green method as the use of harmful carcinogenic chemicals is largely avoided.

Chelating resins based on Amberlite XAD-16 with dipicolylamine for lead and copper have been reported by Chauhan *et al*. [14]. They observed that this chelating resin has more than 97.9% efficiency in removing Pb(II) and Cu(II) from industries' wastewater samples. Elbadawy *et al*. [15] also studied the adsorption capacities of Amberlite XAD-16 based chelating resin 1,8-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate for the Pb(II) and Cd(II) from aqueous solutions. Cao *et al*. [16] have developed a similar chelating resin based on polystyrene-poly(hydroxamic acid) copolymer for adsorption of rare earth elements. They found that this resin has a large adsorption capacity for La(III), Ce(III) and Y(III) ions. *tert*-Butyl 2-picolylamino-*N*-acetate (AMPY) immobilized on polystyrene has been synthesized by Qiu *et al*. [17] and used to remove trace copper. The amount of copper was determined by AAS and also studied the resin and Cu (II) interactions by X-ray photoelectron spectroscopy (XPS). The adsorption was found to be an endothermic and spontaneous process and also pseudo-second-order.

However, chelating resins based on organic long-chain polymers have the disadvantage that they have a high tendency to absorb water and swell. They also are non-biodegradable, so they may accumulate in the landfills after being discarded

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and may cause more harm than good to the environment. Many chelating resins based on biopolymers, cellulose, chitosan and silica gel [18-20] have been developed to overcome this problem. These biopolymers are readily available, economical and biodegradable.

The chelating material based on cellulose having chemically bonded iminodiacetate functional groups was used to preconcentrate trace metals in aqueous samples [21]. Cellulose modified with dithiocarbamate (DMC) was used for the separation of precious metals [22]. A biopolymer-based chelating resin with N-methyl-D-glucamine onto the surface of chitosan (CTS-MS) has been synthesized by Wu *et al*. [23] to separate boron and its subsequent analysis using UV spectrophotometer. This CTS-MS resin was highly selective for boron and its absorption capacity also remained constant after 5 cycles, indicating that it can be reused.

Silica gel-based chelating adsorbent with covalently bonded pyrrolidine dithiocarbamate has been synthesized and used for Hg(II) ions [24]. The adsorption capacity was studied by X-ray photoelectron spectroscopy (XPS) and found that the modified silica gel has a very high adsorption capacity in comparison to unmodified silica gel. Silica-gel chemically modified with ethylenediaminetriacetate was also used to preconcentrate actinides and lanthanides [25].

Aurintricarboxylic acid (ATA), a triphenylmethane dye is obtained when salicylic acid is treated with sulphuric acid, formaldehyde and sodium nitrite [26,27]. It has been widely used as an analytical reagent and a potent inhibitor of many biochemical processes. In present work, we have used silica gel as solid support for covalently immobilizing aurintricarboxylic acid and optimized the conditions for the quantitative sorption of Ni(II) and Cd(II) ions. The current method is employed for the separation and preconcentration of these ions in some real and water samples, both by batch and column techniques.

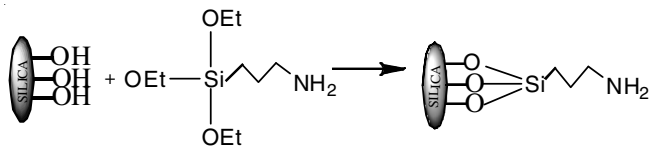
EXPERIMENTAL

Aurintricarboxylic acid (ATA) (BDH England) was used without further purification. The stock solutions of Ni(II) and Cd(II) were prepared by dissolving corresponding sulphate salts in double-distilled water and standardized complexometrically using standard EDTA solution [28]. 3-Aminopropyltriethoxy silane (APTES) was procured from Sigma-Aldrich (India).

Instrumentation: The pH measurements were carried out using ECIL digital pH meter (model 5651). ECIL 4136 atomic absorption spectrometer was used for the determination of metal ions. For determination of IR spectra, Perkin-Elmer Spectrum 2000 FTIR spectrometer was used. For performing column experiment, a 50 cm long glass column with an internal diameter of 1 cm was used. Batch experiments were carried out in a double-walled jacket at the constant temperature (25 ºC) maintained by the Julabo F-20 thermostat.

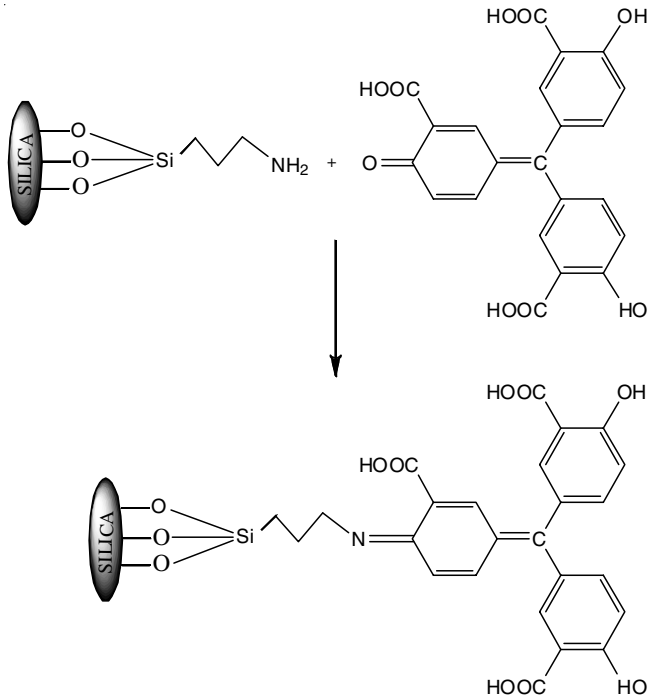
Aurintricarboxylic acid (ATA) immobilized silica gel (SG-ATA): ATA was immobilized on silica gel in two separate steps [29,30] as follows:

Step-I: Functionalization of silica gel: In a double-necked round-bottom flask, 25.0 g activated silica gel was taken. To this 100 mL of 10% (v/v) 3-aminopropyltriethoxysilane in dry toluene was added. The mixture was refluxed in the nitrogen atmosphere for 12 h with constant stirring. The functionalized silica gel, *i.e.* aminopropyl silica gel (APSG), was then washed with toluene, ethanol and acetone and dried in a vacuum oven at 75 ºC for 10 h (**Scheme-I**).



Scheme-I: Functionalization of silica gel with $-NH_2$ group

Step-II: Immobilization of aurintricarboxylic acid on silica gel (SG-ATA): Aurintricarboxylic acid (ATA, 2.0 g) was dissolved in dry ethanol and was treated with APSG (10.0 g) for 8 h with constant stirring. The ATA immobilized on silica gel (SG-ATA) was filtered, washed and heated for 8 h at 55 ºC in a vacuum line (**Scheme-II**).



Scheme-II: Immobilization of aurintricarboxylic acid on silica gel

The immobilization of ATA on silica gel was confirmed by IR spectroscopy.

Procedure for separation of metal ions: Both batch and column experiments were used for the separation and preconcentration of metal ions using aurintricarboxylic acid on immobilized silica gel (SG-ATA).

Batch experiment: Modified silica gel (SG-ATA, 0.05 g) was placed in a double-walled glass jacket attached to a thermostat. A metal ion solution (25.0 mL, 5.0 μg mL^{-1}) was added to SG-ATA. With the help of sodium acetate-acetic acid buffer, these metal ion solutions were previously maintained at the required pH. A constant temperature of 25 ºC was maintained in the flask for 15 min. After the immobilized silica gel settled

down, the supernatant solution was separated and atomic absorption spectroscopy (AAS) was used to measure the metal ions adsorbed by the modified silica gel. The differential analysis determined the metal ions adsorbed by the immobilized silica gel.

Column experiment: Columns were packed with 0.05 g of immobilized silica gel. Approximately 5 mL of buffer solution (pH = 3.0 to 9.0 depending on the optimal pH range of the metal ion for maximum complexation) was passed through these columns. Flow rates of 2.0 mL/min were used to pass the solution of metal ions (5.0 μg mL^{-1}), which were kept at those pH values as those of columns. A 0.1 M HCl was used to elute the metal ions adsorbed to the modified silica gel. An atomic absorption spectrometer (AAS) was used to measure the metal ions in the eluent.

RESULTS AND DISCUSSION

The IR spectra of SG-ATA show a band at 1580 cm^{-1}, which is the major characteristic of ν(C=N). However, the benzene ring vibrations and deformation modes of the -CH_2 group were observed between 1570-1420 cm^{-1}.

Effect of pH: Using a column experiment, the effect of pH on the adsorption of metal ions by SG-ATA is investigated. Fig. 1 shows the effect of pH on metal ion recovery by modified silica gel. In case of nickel, maximum adsorption has occurred in the pH range 5.7-7.0 with a recovery of 99%, while for cadmium this pH range was 5.9-7.8 with a recovery of 90%. The decrease in uptake of metal ions at higher pH may be attributed to hydrolysis of these ions, while at lower pH, H^+ competes more than these ions. We used these pH ranges for carrying out the rest of the experiments.

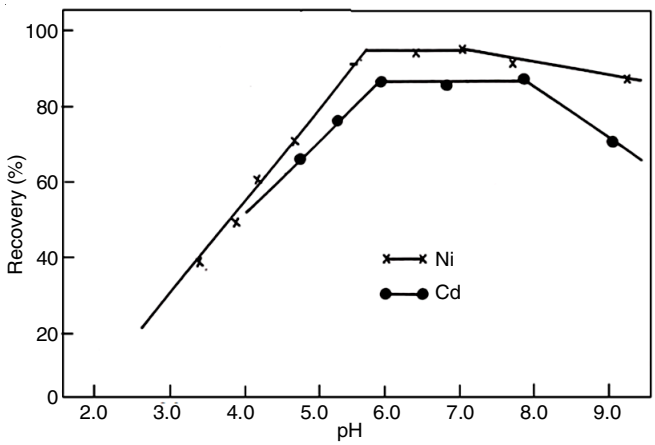


Fig. 1. Effect of pH on the adsorption of metal ions by SG-ATA

Optimization of adsorption time: Batch experiments were used to determine the time for a solid-liquid system to reach equilibrium. Metal ion solutions were maintained at the desired pH values and equilibrated with SG-ATA for different time intervals (from 2 to 30 min). After the modified silica gel settled down, the supernatant solution was removed. Metal ions adsorbed on the chelating silica gel were determined based on the difference in amounts of metal ions in solution and supernatant. Fig. 2 shows the plot of the percentage of Ni(II) and Cd(II) adsorbed *versus* time, indicating fast metal ion exchange kinetics for the uptake of these ions by SG-ATA. It was found that the time required to reach the equilibrium is about 5 min for Ni(II) and 8 min for Cd(II).

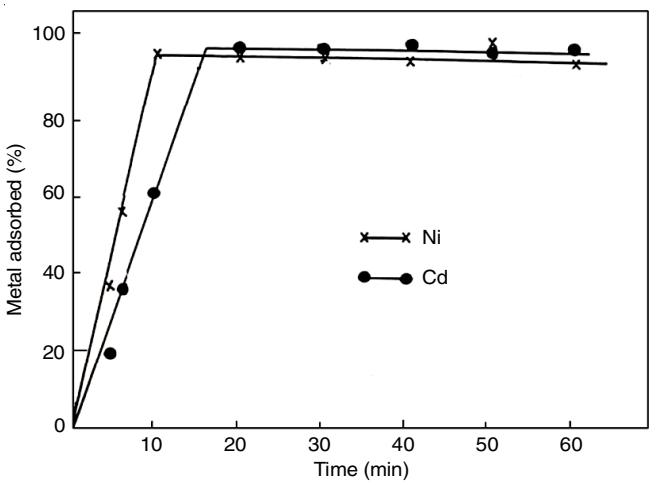


Fig. 2. Effect of time on the recovery of metal ions by aurintricarboxylic acid modified silica gel

Effect of amount of modified silica gel: The amount of immobilized silica gel for quantitative uptake of metal ions was studied by the batch method by using different amounts of immobilized silica gel. Ni(II) and Cd(II) ion solutions (5.0 μg mL^{-1}) maintained at the desired pH were stirred with different amounts of SG-ATA (between 0.01-0.08 g) in a thermostated double-walled glass jacket at 25 ºC for 15 min. The supernatant solution was removed after the modified silica gel settled. Metal ions adsorbed on the chelating silica gel were determined based on the difference in amounts of metal ions in solution and supernatant. Fig. 3 shows that the adsorption of nickel was found to be maximum and constant when 0.05 g of modified silica gel was used, while for Cd(II), a minimum of 0.03 g of modified silica gel has to be used for quantitative adsorption. However, for simplicity, further experiment was carried out with a minimum of 0.05 g of ATA modified silica gel.

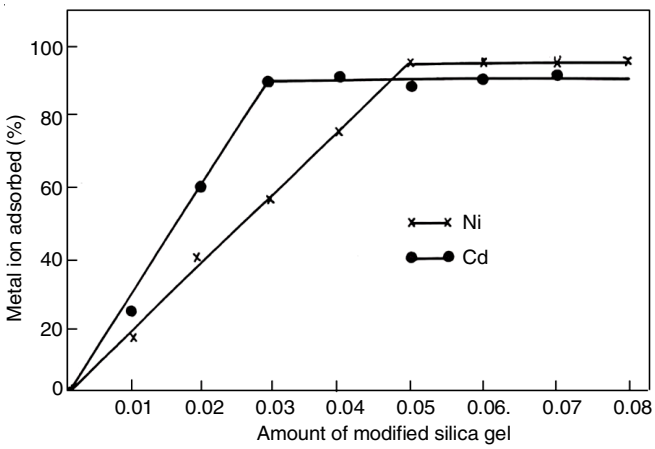


Fig. 3. Effect of amount of aurintricarboxylic acid modified silica gel on the recovery of metal ions

Effect of flow rate: The influence of flow rate of metal ion solutions on the ability of chelating silica gel to adsorb

Ni(II) and Cd(II) is investigated. Flow rates of 0.5-5.0 mL/min were employed to pass 10.0 mL of metal ions (5.0 μg mL^{-1}) along with columns of modified silica gel at the pH of maximum complexation. On passing 10 mL of 0.1 M HCl through the column, the metal complexed to SG-ATA is removed and quantified by AAS in that solution. Adsorption of these ions was quantitative and reproducible in this range. However, the flow rate was maintained at 2 mL per minute for further studies.

Effect of temperature: Adsorption of metal ions was found to be affected by temperature. By batch experiment, the influence of temperature on silica gel adsorption of metal ions was studied. In this study, 10.0 mL (5.0 μg mL^{-1}) of Ni(II) and Cd(II) metal ions were placed in a double-walled glass jacket attached to a thermostat and stirred for 15 min at different temperatures (between 15 and 55 ºC). Fig. 4 shows the change in percent adsorption of metal ions (nickel and cadmium) with temperature. The percent adsorption of Cd(II) metal ions was constant and quantitative up to 40 ºC, while for Ni(II), this temperature was 35 ºC and decreased during the experiment.

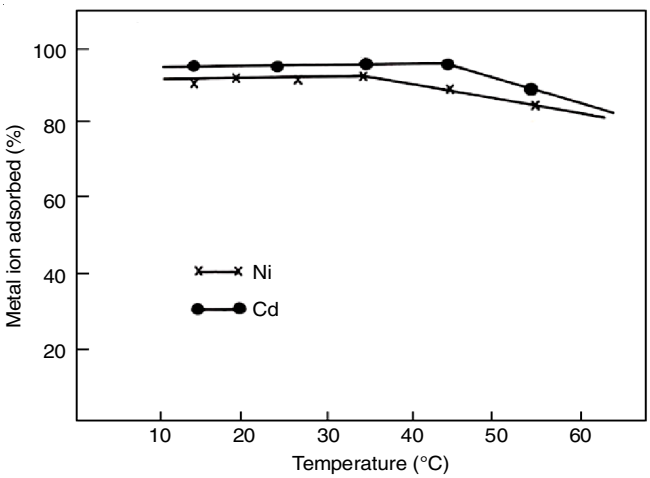


Fig. 4. Effect of temperature on the recovery of metal ions by aurintricarboxylic acid modified silica gel

Adsorption isotherms: Adsorption isotherms at 25 ºC for Ni(II) and Cd(II) in the concentration range of 3.0×10^{-5} to 1.6×10^{-3} mmol mL^{-1}, using a batch technique, Solutions of these metal ions were stirred with a fixed amount of SG-ATA for 15 min at the desired pH values and AAS was used to determine the metal content of each supernatant solution after appropriate dilutions of each flask. Fig. 5 shows Ni(II) and Cd(II) adsorption isotherms. The following equation was used to calculate the amount of metal adsorbed:

$$N_f = \frac{(x - y)}{z}$$

where N_f = amount of metal ions adsorbed per g of SG-ATA (in mmol g^{-1}); x and y are the initial amounts of metal ions and amount of metal ions in the supernatant, respectively (mmol) and z is the amount of SG-ATA (g).

The distribution coefficient, $D = N_f/C$, was calculated, where N_f is expressed in mmol g^{-1} and C, the concentration in mmol mL^{-1}. The average value of D calculated for each metal ion (mL g^{-1}) are Ni(II): 2.85×10^2 and Cd(II): 2.91×10^2.

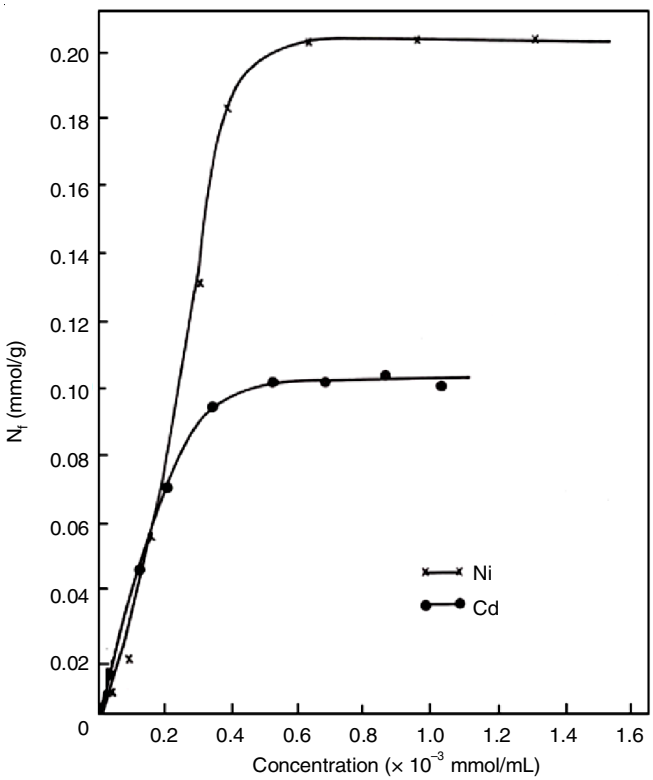


Fig. 5. Adsorption Isotherm of metal ions at 25 °C

Effect of electrolytes: The effect of various electrolytes, like sodium chloride, potassium chloride, sodium nitrate and potassium nitrate, on adsorption of metal ions by ATA modified silica was studied with the help of the column experiment. It was found that these electrolytes did not affect the uptake of Ni(II) and Cd(II) by SG-ATA.

Pre-concentration and recovery of metal ions: Preconcentration of metal ions was studied by the column method. A 1000 mL of metal ion solution (0.05 μg mL^{-1}), maintained at pH of maximum complexation, was passed through a column packed with 0.50 g of ATA resin. The metal adsorbed was eluted with 10 mL of 0.1 M HCl and subsequently, the metal ion in the eluent was determined by AAS. The mean of five determinations of Ni(II) concentration was found to be 4.90 ± 0.19 μg mL^{-1} with a recovery of 98%, while for Cd(II), the concentration in the eluent was found to be 4.65 ± 0.22 μg mL^{-1} and recovery of ~ 92%. The preconcentration factor (PF) was 100 in each case, indicating that this ATA resin can effectively separate and preconcentrate these metal ions from the matrix component prior to their determination by AAS.

Analytical performance of the method: The calibration curves were drawn for Ni(II) and Cd(II). This was done by direct aspiration of the metal ion solutions (0.10-10.00 μg mL^{-1}) in FAAS [20,31,32]. Calibration equations, calculated based on the average of triplicate readings for each standard solution, were found to be A = 0.4193 C + 0.0129 [for Ni(II)] and A = 0.1397C + 0.0143 [for Cd(II)], where A is the absorbance and C is the concentration of metal ions in μg mL^{-1}. The correlation coefficient (R^2) of the calibration curve equation obtained was 0.9998 (for Ni^{2+}) and 0.9996 (for Cd^{2+}), which indicated a good linearity in the mentioned concentration range.

The instrumental detection limit was determined by passing 50 mL of blank solutions (prepared by adding minimum amount of these metal ions to water and adjusted to the pH of maximum complexation) through the column. The column was washed with 50 mL of 0.1 M HCl (as there is no preconcentration). The instrumental detection limit based on the mean of blank values plus three-times the standard deviation of the blank values was 0.17 μg mL^{-1} for nickel and 0.19 μg mL^{-1} for cadmium (N = 20). The analytical detection limit (ADL) was calculated by dividing the instrumental detection limit by the preconcentration factor (100). The ADL was found to be 1.70 μg mL^{-1} and 1.90 μg mL^{-1} for nickel and cadmium, respectively (Table-1).

TABLE-1
ANALYTICAL CHARACTERISTICS OF THE PROPOSED METHOD FOR COPPER AND NICKEL

	Ni(II)	Cd(II)
pH for quantitative recovery	5.7-7.0	5.9-7.8
Amount of resin (g)	0.05	0.05
Flow rate of solution (mL min^{-1})	2.0	2.0
Temperature	Upto 35 °C	Upto 40 °C
Pre-concentration factor	100	100
Sorption capacity (mmol g^{-1})	0.21	0.10
Recovery (n = 5, at 5 μg mL^{-1})	4.90 ± 0.19	4.65 ± 0.22
Instrumental detection limit (N = 20) (μg mL^{-1})	0.17	0.19
Analytical detection limit (N = 20) (μg L^{-1})	1.70	1.90
Linear range (μg mL^{-1})	0.10–10.00	0.10–10.00
Calibration equation	A = 0.4193 C + 0.0129	A= 0.1397 C + 0.0143

A: absorbance, C: metal ion concentration in ppm

Analytical applications of aurintricarboxylic acid (ATA) immobilized silica gel (SG-ATA): The applicability of SG-ATA for analysis of Ni(II) and Cd(II) ions present in real samples was carried out by separating and pre-concentrating these ions present in the alloy, synthetic water samples (spiked with Cd(II)) and in cigarette samples.

Determination of nickel in alloy samples: Alloy sample (0.1 g) was taken in a 250 mL conical flask and 15.0 mL of aqua-regia was added. The solution was heated at low temperature on a hot plate nearly to dryness. The nitrates in the residue were expelled by heating the residue with 5.0 mL conc. HCl. The process was repeated to ensure the complete removal of nitrates. The resulting residue was dissolved in a minimum amount of distilled water, and the resulting solution was made to 100 mL. After pH adjustment with acetate buffer, an aliquot of 4 mL was diluted to 500 mL. This sample (10 mL) was then passed through an SG-ATA-packed column at a flow rate of 2 mL min^{-1}. On passing 0.1 M HCl through this column, Ni(II) taken up by SG-ATA was desorbed and its amount in this solution was determined with the help of AAS. The results of the above experiment are given in Table-2.

Determination of cadmium in the water sample: The water sample (spiked with cadmium) and adjusted to desired pH value was passed through the column packed with SG-ATA. The adsorbed metal ion was eluted from the column with 0.1 M HCl and the amount of cadmium in this solution was determined with the help of the AAS technique. Table-3 shows that cadmium can be effectively preconcentrated and determined in water samples even if it contains cadmium at ppb level.

TABLE-3
DETERMINATION OF Cd(II) IN WATER SAMPLES (SPIKED WITH Cd(II) IONS)

Volume of sample (mL)	Volume of eluent (mL)	Amount of Cd(II) in eluent* (μg mL^{-1})	Amount of Cd(II) in water sample (μg mL^{-1})	Standard deviation
100.0	10.0	0.19	0.019	0.09

*Mean of five determinations

Determination of cadmium in cigarette sample: The cigarette sample was prepared as discussed earlier [33]. A sample solution (10.0 mL) was then passed through a column packed with SG-ATA. The adsorbed metal ion was then eluted from the column with 10.0 mL of 0.1 M HCl and The AAS technique was used to determine cadmium in the eluent. Results are given in Table-4.

TABLE-4
DETERMINATION OF Cd(II) PRESENT IN CIGARETTE SAMPLES

Volume of sample (mL)	Volume of eluent (mL)	Amount of Cd(II) recovered* (μg mL^{-1})	Standard deviation
100.0	10.0	0.11	0.16

*Mean of five determinations

Conclusion

Silica gel-based chelating resin with immobilized aurintricarboxylic acid (ATA) offers an environment-friendly method for separating and preconcentrating trace amounts of Ni(II) and Cd(II). If determined directly using a flame atomic absorption spectrometer, the sample matrix causes interferences in determining these ions. The time required for equilibration is small and offers a suitable temperature range for estimation. The pH range is sufficiently large enough for quantitative estimation of these ions. The method was successfully employed for the determination of Ni(II) in alloy samples and Cd(II) in water and cigarette samples.

TABLE-2
DETERMINATION OF Ni(II) IN ALLOY SAMPLES

Sample	Certified composition (%)	Ni taken (%)	Ni found* (%)	Standard deviation
A (CM 247 LC)	Cr (8.1), Mo (0.5), Al (5.6), Ta (3.2), Zr (0.015), C (0.06), Co (9.0), W (9.5), Ti (0.7), Hf (1.40, B (0.015), Ni (61.91)	61.91	60.05	0.82
B (IN 718)	Cr (18.0), Mo (3.0), Fe (19.0), Co (5.1), Ni (54.9)	54.90	50.92	0.56

*Mean of five determinations

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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