Octadecyl bonded silica membrane disk modified with Cyanex302 for separation and flame atomic absorption spectrometric determination of nickel from tap water and industrial effluent

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ABSTRACT

A simple and reliable method based upon impregnation of Cyanex302 on octadecyl bonded silica membrane disk has been developed for separation and atomic absorption spectrometric determination of nickel. The influence of various parameters like aqueous phase pH, flow rate and volume of eluent were investigated systematically to optimize the conditions for quantitative sorption and desorption of nickel. The break through volume for nickel was greater than $1.0\,dm^3$, enrichment factor more than 100 and a detection limit of $2.1\,\mu g\,dm^{-3}$ was achieved. The method applied for detection of nickel in tap water and effluent sample had a relative standard deviation (R.S.D.) of 0.4%.

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1. Introduction

Surface fresh waters and drinking waters are likely to contain less than $2\,\mu g\,dm^{-3}$ nickel [1]. Nickel enters aquatic systems through anthropogenic activities such as mining, smelting, refining, alloy production, plating, fuel combustion, waste incineration, etc or through the discharge of effluents bearing nickel. The elevated level of nickel in the environment is a cause for alarm due to its allergic reaction, carcinogenic, and toxic effects [2]. Hence, its determination not only from water, but also from soil, sediments, food products, etc., has significance.

For accurate and sensitive detection of trace elements in presence of matrix elements, a separation and preconcentration step is a prerequisite. As, instruments like flame atomic absorption spectrometry (FAAS) or inductively coupled plasma atomic-emission spectrometry (ICP-AES) do not match the detection limits for analysis at micro-and sub-micro levels. Over the years, solid phase extraction (SPE) has emerged as an alternative technique over solvent extraction and ion exchange, as it offers better advantages in terms of cost effectiveness, simplicity, rapidity, flexibility and eco-friendliness, along with the availability of large number of sorbents.

SPE methods for separation of trace level of nickel using C 18 disk [3,4], silica gel [5–7], Amberlite series resins [8–14], Merrifield's chloromethylated styrene divinylbenzene resin [15], Ambersorb

and chromosorb resins [16–18], activated carbon [19,20], cellulose [21], naphthalene [22], and polyurethane foam [23] have been developed. Different methodologies have been adopted to achieve the desired enrichment factors for analysis of samples containing low concentrations of nickel. Several solid phase extraction methods have been devised for nickel determination in various food and water samples. Silica gel was modified with gallic acid through -NH₂ after its silanization using aminopropyl silane [5]. Polymeric resins viz., XAD-2 [8], XAD-16 [11], XAD-1180 [14], chloromethylated styrene divinylbenzene [15], and polyurethane foam [23] were functionalized through –N=N– spacer using pyrocatechol, nitrosonaphthol, 1,4-dihydroxyanthraquinone, 1-(2-pyridylazo)-2-naphthol, *p-tert*-butylcalix[4]arene-1,2-crown-4, and α-naphthol, respectively. Nickel was determined in fuel ethanol using cellulose modified with *p*-aminobenzoic acid [24]. From a sample solution, nickel was selectively adsorbed on XAD-2000, XAD-2010, Ambersorb 572 and activated carbon as its diethyl dithiocarbamate [25,26], EDTA [16], and 1,10-phenanthroline [19] complex, respectively. Impregnation of ammonium pyrrolidine dithiocarbamate, and piperidine dithiocarbamate on Amberlite XAD-7 [13], 4,6-dihydroxy-2-mercaptopyrimidine on activated carbon [20] and C 18 disk with 5-(6-methoxybenzothioazoleazo)-8-aminoquinoline [3] was reported for SPE of nickel in different water samples.

Nickel is used in nickel plating plants, silver refineries, zinc base casting industries, storage batteries, porcelain enameling, copper sulfate manufacture, mineral processing, etc. The treatment of wastes or effluents generated from such industries is necessary

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Table 1
Optimum condition for solid phase extraction of nickel.

Sr. no.	Parameters	Observations
1	Flame atomic absorption spectrometry	Wave length = 232.0 nm, slit = 0.2, flame = air–acetylene; oxidizing; lean blue
2	Amount of Cyanex302	30 mg
3	Aqueous phase	pH 5.5
4	Aqueous phase flow rate	10.0 cm^3 min^{-1}
5	Eluent	1.0 M HNO$_3$
6	Eluent volume	10 cm^3
7	Eluent flow rate	10.0 cm^3 min^{-1}
8	Sample break through volume	>1.0 dm^3
9	Preconcentration factor	>100
10	Lower limit of detection	2.1 μg dm^{-3}

to meet the discharge norms for nickel (2.0 mg dm^{-3}) as per legal requirements of US Environmental Protection Act.

It is desirable to develop new SPE methods with sorbents which are easy to prepare, exhibit good reusability, enable rapid separation of desired analyte with high preconcentration factors, and can be performed in any laboratory and not restricted only to sophisticated instruments.

In view of this, a simple method based upon the impregnation of Cyanex302 {(bis (2,4,4-trimethyl pentyl)monothiophosphinic acid} on C 18 disk is proposed for separation and determination of nickel in tap water and effluent sample is presented.

2. Experimental

2.1. Instrumentation

A PerkinElmer atomic absorption spectrophotometer AAnalyst200 was employed for determining metal ion concentration. An Elico LI-120 digital pH meter Elico India Ltd., was used for pH adjustments. A Millipore vacuum pump was used for maintaining the sample flow rates.

2.2. Chemicals and reagents

A stock solution of nickel (1 mg cm^{-3}) was prepared by dissolving appropriate quantity of nickel metal powder (Sisco Chemicals Ltd.) in slightly acidified distilled water. The solution was standardized volumetrically [27], and a working solution containing 20 μg cm^{-3} nickel was prepared by appropriate dilution. 3 M Empore membrane disks (47 mm diameter and 0.5 mm thick, 10% PTFE fibrillated) containing octadecyl bonded silica (8 mm particle, 60-Å pore size), distributed by Varian India Ltd. were used in conjunction with standard 47 mm filtration apparatus. Cyanex302 obtained as a gift sample from Cytec Canada was used without further purification. All chemicals and reagents used were of A.R. grade.

2.3. Preparation of impregnated octadecyl bonded silica membrane disk

The Cyanex302 impregnated octadecyl bonded silica membrane disk was prepared as mentioned earlier [28].

2.4. Solid phase extraction, preconcentration procedure

Impregnated C 18 disk was preconditioned with 50 cm^3 of double distilled water adjusted to pH 5.5 using 1.0 M HNO$_3$ or 1:1 NH$_3$. A 50 cm^3 sample solution containing 20 μg nickel, was adjusted to a pH 5.5 with 1.0 M HNO$_3$ or 1:1 NH$_3$ and passed through the disk
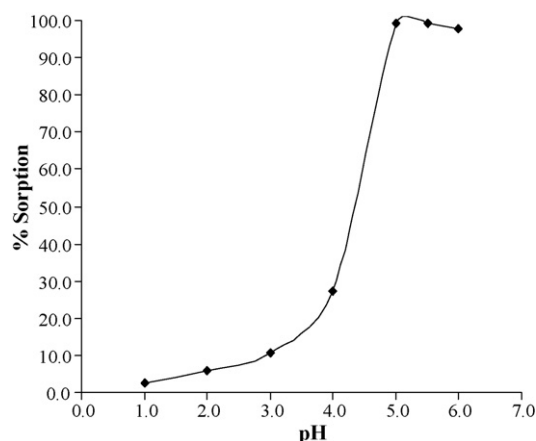
Fig. 1. Effect of aqueous phase pH on sorption of nickel, conditions: aqueous phase = 20 μg Ni(II) in 50 cm^3, flow rate = 10.0 cm^3 min^{-1}.

at a 10.0 cm^3 min^{-1} flow rate. Nickel eluted from the modified disk with 1.0 M HNO$_3$ at a flow rate of 10.0 cm^3 min^{-1} was analyzed by flame atomic absorption spectrophotometer (FAAS) using a calibration curve. The optimum sorption and desorption parameters for nickel are presented in Table 1. The reproducibility of the method evaluated for nickel determination in six replicate experiments had a R.S.D. of 0.4%.

3. Results and discussion

3.1. Effect of aqueous phase pH and flow rate

Nickel sorption was studied in the pH range 1.0–6.0. The pH was adjusted with 1.0 M HNO$_3$ or 1:1 NH$_3$. Nickel was eluted from the disks with 1.0 M HNO$_3$ and determined by FAAS. The sorption of nickel was quantitative (% sorption = 99.0 ± 0.4) between the pH 5.0–6.0 (Fig. 1). As the cation exchange process is operative with Cyanex302, its lower sorption at pH values below 4.0 may be attributed to the formation of non-cationic nickel species. Higher pH values (>6.0) were not tested due to the possible hydrolysis of silica.

The influence of sample flow rate on nickel uptake by the disk at pH 5.5 was studied. It was found that sorption of the metal ion was quantitative (99.0 ± 0.4%) and reproducible using an aqueous phase flow rate of 8.0–10.0 cm^3 min^{-1}. However at a flow rate greater than 15.0 cm^3 min^{-1}, the sorption of nickel was 98.0 ± 0.8%, possibly due to its insufficient contact with the sorbent. Hence, the optimum aqueous phase conditions used were pH 5.5 at a sample flow rate of 8.0–10.0 cm^3 min^{-1}.
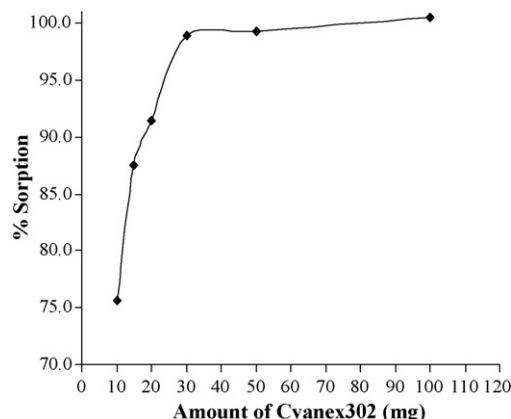
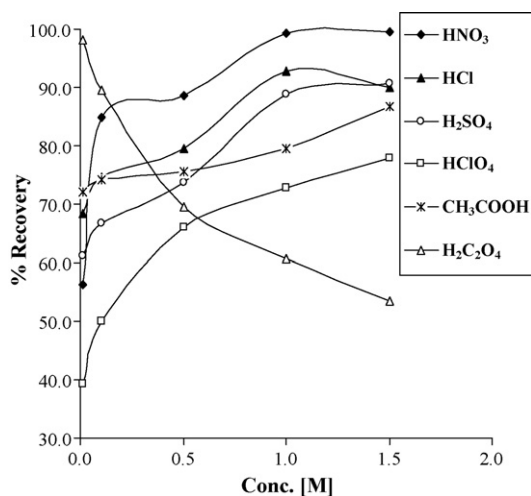**Fig. 2.** Effect of amount of Cyanex302 on sorption of nickel.

Fig. 3. Effect of eluents on recovery of nickel, conditions: eluent = 10 cm^3, flow rate = 10.0 cm^3 min^{-1}.

3.2. Effect of amount of Cyanex302

A 50 cm^3 sample solution containing nickel (20 μg) adjusted to pH 5.5 was studied for its sorption with C 18 disk modified with 10–100 mg of Cyanex302 (Fig. 2). Amount of Cyanex302 lower than 30 mg resulted in incomplete sorption of nickel. The minimum quantity of Cyanex302 required for quantitative sorption of nickel was 30 mg. Hence for subsequent studies 30 mg Cyanex302 sorbed on C 18 disk was used.

3.3. Choice of eluent

In order to choose the most effective eluent for recovery of nickel (20 μg) sorbed on Cyanex302 (30 mg impregnated on C 18 disk), different eluents were studied (Fig. 3). The most effective eluent for nickel was 1.0 M HNO$_3$. Hence using different volumes and flow rates of 1.0 M HNO$_3$, elution studies were carried out and are summarized in Table 2. Quantitative recovery of nickel was achieved using 10 cm^3, 1.0 M HNO$_3$. Hence 10 cm^3, 1.0 M HNO$_3$ at a flow rate of 10 cm^3 min^{-1} was used as an eluent for further studies.

4. Analytical performance

4.1. Reusability of the disk

The stability and potential reusability of the modified disk was accessed by monitoring recovery of nickel for several cycles. Using the same disk the preconcentration procedure for sorption and desorption of nickel under the optimum conditions was

Table 2
Effect of eluent volume and flow rate.

Sr. no.	Volume of 1.0 M HNO$_3$[a] (cm^3)	% Recovery
1	5	69.2 ± 0.7
2	10	99.0 ± 0.4
3	15	99.4 ± 0.0
4	20	99.2 ± 0.1

Sr. no.	Flow rate of 10 cm^3, 1.0 M HNO$_3$[b] (cm^3 min^{-1})	% Recovery
1	5	99.3 ± 0.1
2	10	99.0 ± 0.4
3	15	89.6 ± 0.3
4	20	75.2 ± 0.5

[a] Eluent flow rate = 10 cm^3 min^{-1}.
[b] Eluent volume = 10 cm^3.

Table 3
Effect of diverse ions.

Sr. no.	Ions	Tolerance limit (μg)
1	Na$^+$	1000
2	K$^+$	1000
3	Ca^{2+}	100
4	Mg^{2+}	100
5	Pb^{2+}	100
6	Cd^{2+}	20
7	Mn^{2+}	20
8	Cr^{6+}	30
9	Cl$^-$	1000
10	F$^-$	1000
11	NO$_3$$^-$	100
12	SO$_4$$^{2-}$	100
13	PO$_4$$^{3-}$	100
14	Ascorbate	100
15	Citrate	100
16	Tartarate	100

Table 4
Analysis of tap water.

Sr. no.	Amount of nickel added (μg)	Amount of nickel recovered (μg)	% Recovery ±a
1	0	2.07	–
2	1	2.99	97.3 ± 0.1
3	5	7.22	99.4 ± 0.1

±a = % R. S. D. of triplicate analysis.

followed (Fig. 4). The recovery of nickel was quantitative and reproducible (99.0 ± 0.4%) up to 15 cycles. This indicates that the modified disk has a good reusability and reliability for continuously usage.

4.2. Breakthrough volume

In SPE methodologies breakthrough volume is an important parameter for detection of low concentrations of metal ion. Different volumes (10–1000) cm^3 of aqueous phase containing nickel were passed through the disk to check the breakthrough volume. The recovery of nickel was tested by the recommended procedure. It was observed that the sorption of nickel was quantitative even from 1000 cm^3. The breakthrough volume is thus greater than 1000 cm^3 and a preconcentration factor of 100 or more using 10 cm^3 eluent to recover nickel, which is comparable with other SPE methods.
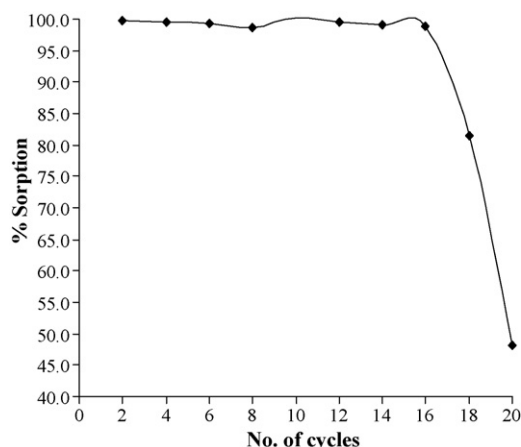

Fig. 4. Reusability of impregnated C 18 disk.

Table 5
Summary of SPE methods for nickel.

Solid support (method for modification of solid support)	Ligand	L.O.D.	P.F.	Reusability (no. of cycles)	Application	Ref.
C-18 disk (I)	5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	$0.06\,\mu g\,L^{-1}$	100	10	Synthetic water, sea water, and river water	[3]
C-18 disk (I)	N,N'-Bis(3-methylsalicylidene) ortho phenylene diamine	30 ng per 1000 mL	–	–	Synthetic water, tap water, and river water	[4]
Silica gel (C)	Gallic acid	$0.92\,\mu g\,L^{-1}$	200	10	Artificial water, river water, and certified river sediment	[5]
Silica gel (C)	Salicylaldoxime	$1.5\,\mu g\,dm^{-3}$	50	10	Electroplating waste	[6]
Silica gel (C)	2,3-Dihydroxy benzaldehyde	$3.06\,\mu g\,L^{-1}$	17	>100	Synthetic salted mixture solution, sea water, river water, and certified sediment	[7]
Amberlite XAD-2 (C)	Pyrocatechol	$0.24\,\mu g\,L^{-1}$	200	12	River and tap water	[8]
Amberlite XAD-16 (C)	2-{[1-(3,4-Dihydroxyphenyl) methylidene]amino}benzoic acid	$1.76\,\mu g\,L^{-1}$	100	10	River water and tap water	[10]
Amberlite XAD-16 (I)	1,4-Dihydroxyanthraquinone	$1 \times 10^{-8}\,mol\,dm^{-3}$	100	–	Synthetic certified water, spiked drinking water, tap water, and well water	[11]
Amberlite XAD-16	Sodium diethyldithio carbamate	$51\,ng\,L^{-1}$	75	–	Artificial sea water, spiked sea water and sea water samples	[12]
Amberlite XAD-4 (I)	Ammonium pyrrolidine dithiocarbamate	$0.4\,\mu g\,L^{-1}$	130	–	Spiked sea water and natural water	[13]
	Piperidine dithiocarbamate	$0.9\,\mu g\,L^{-1}$	120	–		
Amberlite XAD-1180 (C)	1-(2-Pyridylazo)-2-naphthol	$1.2\,\mu g\,L^{-1}$	100	11	Certified river sediment, tap, rain, and stream waters	[14]
Merrifield chloromethylated resin (C)	p-$tert$-Butylcalix[4]arene-1,2-crown-4	$1.68\,\mu g\,L^{-1}$	125	12	Standard reference material of soil	[15]
Ambersorb 572	EDTA	$1.42\,\mu g\,L^{-1}$	50	–	Certified tea leaves, parsley, green onion, waste water, and sea water	[16]
Chromosorb 108	Bathocuproinedisulfonic acid	$0.44\,\mu g\,L^{-1}$	80	200	Certified river water, certified apple leaves, certified tea, tap, river, artificial sea water, red wine, rice, black tea, and honey	[17]
Chromosorb 103	8-Hydroxyquinoline	–	125	–	River water and certified bovine liver	[18]
Activated carbon	1,10-Phenanthroline	$24.6\,\mu g\,L^{-1}$	50	–	Certified oriental tobacco leaves and potatoes	[19]
Activated carbon (I)	4,6-Dihydroxy-2-mercaptopyrimidine	$3.5\,\mu g\,L^{-1}$	260	–	Drinking water, spinach leaves, spiked liver, and spiked spring water	[20]
Cellulose (C)	Pyrocatechol	$5.51\,\mu g\,L^{-1}$	75	–	Tap water and river water	[21]
Naphthalene (C)	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol Tetraphenyl borate	$0.04\,\mu g\,L^{-1}$	65	–	Certified water, certified human hair, waste water, and commercial mineral water	[22]
Polyurethane foam (C)	α-Naphthol	$7.01 \times 10^{-5}\,mg\,L^{-1}$	–	–	Certified cast iron, granite, and hematite iron	[23]
C-18 disk (I)	Cyanex302	$2.1\,\mu g\,dm^{-3}$	>100	15	Tap water and industrial effluent	This work

(I): impregnation, (C): chemical modification, L.O.D.: limit of detection, P.F.: preconcentration factor.

4.3. Limit of detection

The limit of detection (LOD) for the determination of nickel studied under the optimal sorption conditions using the proposed method was $2.1\,\mu g\,dm^{-3}$. The LOD was obtained from $C_{LOD} = K S_b\,m^{-1}$ [28] where S_b is the standard deviation of the blank measurements (20 replicates), m is the slope of the linear calibration graph and K is a confidence factor equal to 3.

4.4. Effect of diverse ions on sorption of nickel

In order to investigate selective sorption and determination of nickel from samples containing diverse ions, its sorption in the presence of other ions under the optimum condition was studied. The effect of the amount of other ion required to cause $99.0 \pm 2\%$ recovery of nickel was used to set the tolerance limit. Good tolerance limits for most of the common ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-} were achieved, indicating the applicability of method to complex samples (Table 3).

5. Analytical applications

5.1. Analysis of tap water and method validation

In order to demonstrate the validity of the method developed, $100\,cm^3$ of tap water sample was spiked with different concentrations of nickel and passed through the modified disk as per the general procedure. The total amount of nickel recovered in the eluent was determined by FAAS (Table 4).

5.2. Determination of nickel in industrial effluent

$100\,cm^3$ of industrial effluent containing $241.6\,\mu g$ nickel was passed through the disk and $105.4\,\mu g$ nickel was recovered as per general procedure. The aqueous phase was again adjusted to pH 5.5 and passed through the disk as per the general procedure such that nickel from the sample solution gets completely sorbed on the modified C 18 disk. The sample contained $2.416\,\mu g\,cm^{-3}$ of nickel while $2.373\,\mu g\,cm^{-3}$ was removed, thus the amount of nickel was lowered to $0.043\,\mu g\,cm^{-3}$, which is consistent with discharge

requirements of effluents containing nickel. Zinc ($1.31\,\mu g\,cm^{-3}$), cadmium ($0.068\,\mu g\,cm^{-3}$), copper ($1.2\,\mu g\,cm^{-3}$), and manganese ($14.0\,\mu g\,cm^{-3}$) present in the effluent sample were also detected along with the nickel using FAAS. The results obtained from the analysis indicate the suitability of developed method to control discharge of nickel by the proposed method.

6. Conclusion

The solid phase extraction process developed for determination of traces of nickel using octadecyl bonded silica membrane disk impregnated with Cyanex302 is simple with a preconcentration factor greater than 100 and detection limit of $2.1\,\mu g\,dm^{-3}$. The method has proven applicability for determination of nickel in tap water and its removal from industrial effluents and compared well with other SPE methods (Table 5). The reusability of the modified disk for continuous usage has an added advantage of minimal waste generation.

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