

Novel analytical reagent for the application of cloud-point preconcentration and flame atomic absorption spectrometric determination of nickel in natural water samples

K. Suvadhan^a, D. Rekha^a, K. Suresh Kumar^a, P. Reddy Prasad^a,
J. Dilip Kumar^a, B. Jayaraj^b, P. Chiranjeevi^{a,*}

^a Environmental Monitoring Laboratory, Department of Chemistry, S.V. University, Tirupati 517502, A.P., India

^b Department of Mathematics, S.V. University, Tirupati 517502, A.P., India

Received 27 June 2006; received in revised form 30 September 2006; accepted 3 October 2006

Available online 10 October 2006

Abstract

Cloud-point extraction was applied as a preconcentration of nickel after formation of complex with newly synthesized *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine, and later determined by flame atomic absorption spectrometry (FAAS) using octyl phenoxy polyethoxy ethanol (Triton X-114) as surfactant. Nickel was complexed with *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine in an aqueous phase and was kept for 15 min in a thermo-stated bath at 40 °C. Separation of the two phases was accomplished by centrifugation for 15 min at 4000 rpm. The chemical variables affecting the cloud-point extraction were evaluated, optimized and successfully applied to the nickel determination in various water samples. Under the optimized conditions, the preconcentration system of 100 ml sample permitted an enhancement factor of 50-fold. The detailed study of various interferences made the method more selective. The detection limits obtained under optimal condition was 0.042 ng ml⁻¹. The extraction efficiency was investigated at different nickel concentrations (2–80 ng ml⁻¹) and good recoveries (99.05–99.93%) were obtained using present method. The proposed method has been applied successfully to the determination of nickel in various water samples and compared with reported method in terms of Student's *t*-test and variance ratio *f*-test which indicate the significance of present method over reported and spectrophotometric methods at 95% confidence level.

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Keywords: Nickel; *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine; Cloud-point extraction-preconcentration (CPE-P); Triton X-114; Flame atomic absorption spectrometry (FAAS); Water samples

1. Introduction

Nickel is the metal component of the enzyme urease and as such considered to be essential to plants and some domestic animals. Compared with other transition metals, Ni is a moderately toxic element. However, it is known that inhalation of Ni and its compounds can lead to serious problems, including cancer of the respiratory system [1–3]. Moreover, Ni can cause a skin disorder known as nickel-eczema [4]. The determination of trace metal ions in natural waters and environmental samples is difficult due to various factors, particularly their

low concentrations and matrix effects. Although the atomic absorption spectrometric (FAAS) method is a powerful analytical tool for determining trace elements in environmental samples, preconcentration and separation techniques combined with FAAS are still necessary. Different chelating agents such as pyrrolidine dithiocarbamate [5], 2-(2-benzothiazolylazo)-2-*p*-cresol (BTAC) [6], diethyldithiocarbamate [7], dithione [8], 1,10-phenanthroline [9], 1-nitroso-2-naphthol [10], etc. have been used to remove and preconcentrate traces of nickel from various samples prior to their determination by FAAS. Separation and preconcentration based on cloud-point extraction (CPE) is becoming an important and practical application in the use of surfactants in analytical chemistry [11,12]. The principle and advantages of CPE have been well established and identified in recent years. The use of preconcentration steps based

* Corresponding author. Tel.: +91 877 2250556; fax: +91 877 2261274.
E-mail address: chiranjeevipattium@gmail.com (P. Chiranjeevi).

on CPE offers a conventional alternative to more conventional extraction systems and permits the design of extraction schemes that are simple, cheap, of high efficiency and of lower toxicity than extractions that use organic solvents. The cloud-point methodology was used to extract and preconcentrate metal ions, after the formation of sparingly water-soluble complexes, as an initial step for their determination by flame atomic absorption spectrometry (FAAS) [13–22] or spectrophotometry [23,24]. The same concept was also employed further speciation of Cr [25–27]. The application of sophisticated instrumentation such as FI-CV-ICP [28], FIA-ICP-MS [29] or ETV-ICP-MS [30] has also been described for the determination of metal species.

The present method was based on the complexation of nickel complexed with *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine in presence of Triton X-114 (non-ionic surfactant) at pH 8.0 ± 0.2 using either HCl or NaOH. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. This is an alternative method to the solid phase extraction and column techniques for the analysis of nickel in various samples of environmental importance.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 2380 atomic absorption spectrometer (AAS) with acetylene flame and hollow cathode lamps were used for the determination of nickel. All instrumental settings and operating condition were tabulated in Table 1. A pH meter, Li-129 Model glass-calomel combination electrode was employed for measuring pH values.

2.2. Reagents

Doubly distilled water and high purity reagents were used for all preparations of the standard and sample solutions. All chemicals were purchased from Merck Chemicals, Mumbai, India. Standard stock solution (1000 mg l^{-1}) of nickel(II) was prepared by dissolving the proper amount of analyte in doubly distilled water in a 100 ml flask. Dilute solutions were prepared by the appropriate dilution of the stock solution daily in doubly distilled water for reference solutions. The non-ionic surfactant, Triton X-114 (Merck Chemicals, Mumbai, India) was used without further purification. The 0.001 M of *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacy-

cloptadecin-15-yl-methanimine was prepared by dissolving 0.0471 g in 10 ml of ethanol and made up to the mark with 100 ml of doubly distilled water in 100 ml standard flask. Equimolar solution of NaOH and HCl were added appropriately to get desirable pH of 8.0 ± 0.2 .

2.3. Synthesis *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine

The solution of 5-amino-1,10-phenanthroline (0.03 g, 0.153 mol) in 50 ml, absolute ethanol was added drop wise to the solution of 4'-formylbenzo-15-crown-5 (0.0471 g, 0.152 mol) in 10 ml absolute ethanol and the mixture was stirred for 9 h at 90°C . The ethanol was evaporated to one-third of the initial volume and petroleum ether was added at room temperature. A bright yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered and then recrystallised from cooled ethanol and it shown in Fig. 1. Yield: 0.016 g (55%), mp $190\text{--}192^\circ\text{C}$. IR (KBr): 1651 ($\text{C}=\text{N}_{\text{phen}}$), 1675 ($\text{C}=\text{N}_{\text{imin}}$), 2953–2876 (CH_{aliph}), 1140 ($\text{C}-\text{O}_{\text{aliph}}$), 1268 ($\text{C}-\text{O}-\text{C}_{\text{arom}}$). $^1\text{H NMR}$ ($\text{DMSO}-d_6$): δ 8.77 (s, H, $\text{H}-\text{C}=\text{N}$) (appeared with D_2O), 3.5–4.3 (m, 16H, $-\text{CH}_2-\text{CH}_2-$) (deformation with D_2O), 7.2–7.6 (m, 9 H, $-\text{H}$). LC-MS: 474 [$M+1$]. Anal. calcd. for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_5$ (474): (%): C, 68.48; H, 5.75; N, 8.87; O, 16.89. Found: C, 68.54; H, 5.59; N, 8.32; O, 16.92. The complexation of the metal with ligand is shown in Fig. 2.

2.4. General procedure

For cloud-point extraction, aliquots of the sample solution containing the analyte, 0.12% (w/v) of Triton X-114 and 0.001 M

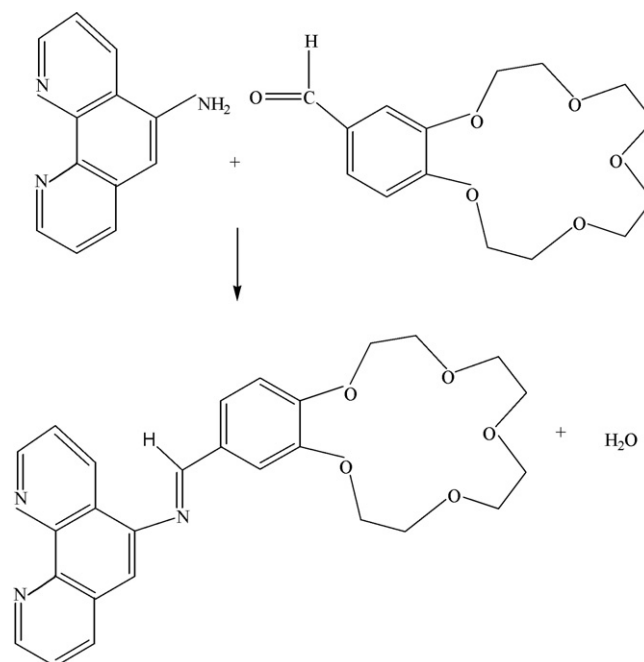


Fig. 1. Synthesis of *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine.

Table 1
Recommended experimental conditions

| | |
|---|-------|
| Analytical wavelength (nm) | 232.0 |
| Lamp current (mA) | 4.0 |
| Air flow rate (l h^{-1}) | 480 |
| Acetylene flow rate (l h^{-1}) | 120 |
| Blow the light path (mm) | 5 |
| Above the burner (mm) | 6 |

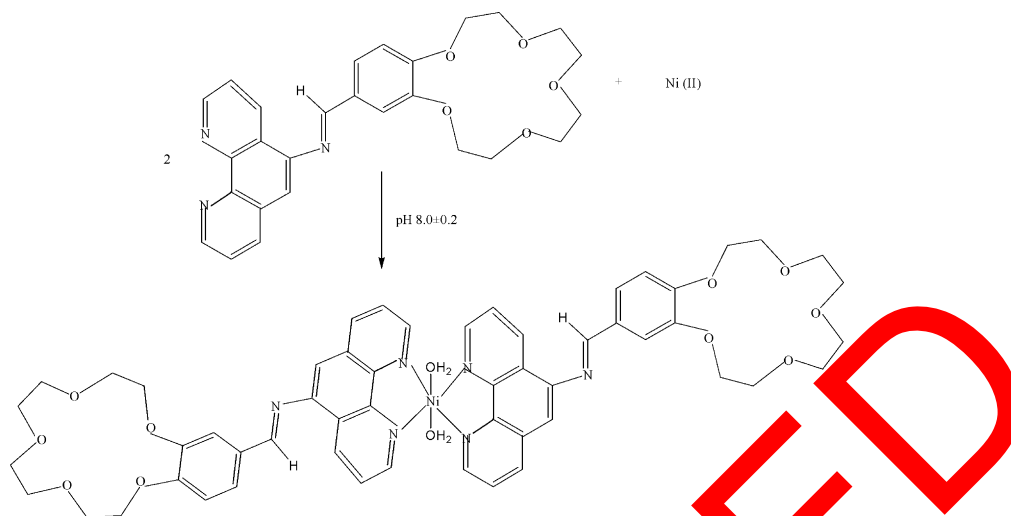


Fig. 2. Nickel complexed with *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine.

N-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine was adjusted to pH 8.0 ± 0.2 with either HCl or NaOH were kept for 15 min in a thermo-stated bath at 40°C . Separation of the two phases was accomplished by centrifugation for 15 min at 4000 rpm. Upon cooling in an ice bath (15 min), the surfactant-rich phase becomes viscous and retained at the bottom of the tube. The bulk aqueous phase was easily decanted and the micellar phase was dissolved in 300 μl of a methanol solution of 0.1 M HNO_3 in order to reduce its viscosity. The final solution was aspirated directly into the flame atomic absorption spectrometry (FAAS).

2.5. Determination of nickel in spiked and natural water samples

The extraction efficiency was studied using spiked water samples for the recovery of nickel. Doubly distilled water was spiked with known amounts of metal standards ($20\text{--}80\text{ ng l}^{-1}$) and allowed to stand overnight. The concentration of nickel in spiked water samples was determined.

Natural water samples were collected around Tirupati area. Tirupati is one of the famous pilgrim center in India and is widely known all over the world. Pollutants are mainly responsible for destroying the natural beauty of the holy town. Ultimately this holy pilgrim center was chosen as the collection area. Several small and medium scale industries are situated in the suburban fringes of Tirupati. The samples are collected from different locations of the study areas. All possible precautions are taken at various stages starting from sample containers, sample collection and storage, processing and analyzing the samples. Water samples (100 ml) filtered through a $0.45\text{ }\mu\text{m}$ cellulose membrane filtered to remove suspended particulate matter. The filtrate contains dissolved organic content do not affect the CPE of the system because the Triton X-114 is a stereo specific for the extraction of metal ligand due to hydrophobic end and were stored at 5°C in metal free poly

ethylene bottle. About 100 ml of water sample was adjusted to pH 8.0 ± 0.2 with HCl or NaOH. About 5 ml of 0.12% (w/v) Triton X-114, 5 ml of 0.001 M *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine and 10 ml of solution containing pH 8.0 ± 0.2 with HCl or NaOH were added. After phase separation, concentrations of metal ion in natural waters were analyzed as described in the above general procedure.

3. Results and discussion

3.1. Effect of pH

Cloud-point extraction of nickel was performed in different pH solutions. The separation of metal ion by the cloud-point method involves prior formation of a complex with sufficient hydrophobic to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Extraction yield depends on the pH at which complex formation is carried out. Fig. 3 shows the effect of pH on extraction of nickel complex. It can be seen that extraction was quantitative for nickel in the pH range of 7.0–9.0. Hence, a pH of 8.0 ± 0.2 was chosen for subsequent investigation.

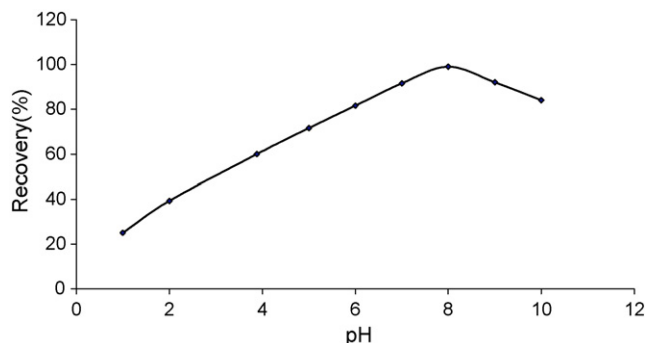


Fig. 3. Effect of pH on the extraction of nickel using cloud-point extraction.

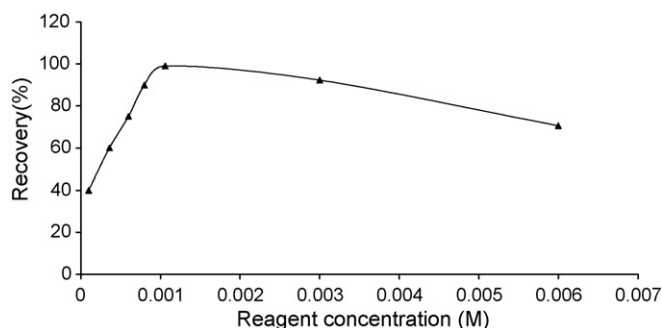


Fig. 4. Effect of *N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine on cloud-point extraction of nickel.

3.2. Effect of *N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine concentration

The effect of *N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine concentration on the determination of nickel was investigated in the range of 0.0001–0.005 M of *N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine. The chelating concentration increased up to certain values, which were sufficient for total complexation and leveled off thereafter. The analytical signal increased up to a *N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine concentration of 0.001 M, which permitted quantitative extraction efficiency. A concentration of 0.001 M was chosen as the optimum concentration for the subsequent studies as presented in Fig. 4.

3.3. Effect of Triton X-114 concentration

The variation in the extraction efficiency upon the surfactant concentration was examined within the following range: Triton X-114 = 0.05–0.15% (w/v). The results are shown in Fig. 5. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud-point temperature and high density of the surfactant-rich phase, which facilitates easy phase separation by centrifugation. The results show that Triton X-114 effectively

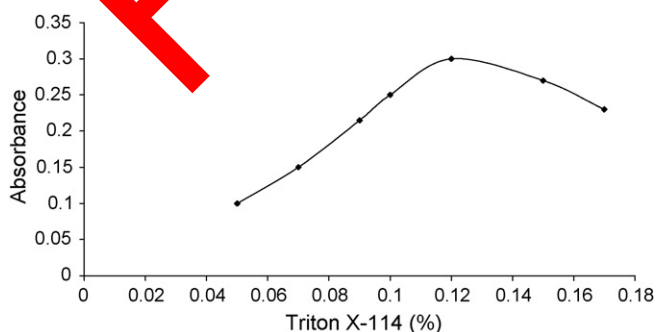


Fig. 5. Effect of Triton X-114 concentration on the analytical signal of nickel using cloud-point extraction.

extracts the nickel from liquid samples at concentration of 0.12% (w/v). With an increase of Triton X-114 concentration above and below 0.12% (w/v), the signals decrease because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. The optimum surfactant concentration used for nickel was the same, 0.12% (w/v) Triton X-114, in order to achieve the optimal analytical signal in conjunction with the highest possible extraction efficiency.

3.4. Effect of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of Ni–*N*-quinolizidine-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine extraction and efficient separation of the phases. The dependence of extraction efficiency upon equilibration temperature and time was studied with the range of 20–60 °C and 5–30 min, respectively. The results showed that an equilibrium temperature of 40 °C and equilibrium time of 15 min was adequate to achieve quantitative extraction.

3.5. Effect of viscosity on the analytical signal and centrifugation time

The presence of methanol and surfactant in the aspirated sample solutions can change the physical properties of the liquid sample by altering the environmental samples [31]. As reported, organic solvent is the flame increases atomization temperature, whilst both organic solvent and surfactant can promote generation of small droplets during nebulization causing positive surface effects. The signal enhancement in the presence of organic solvents has been widely applied to increase the sensitivity during the analysis of a variety of metallic ions [32].

The effect of centrifugation time upon extraction efficiency was studied for the range 5–20 min. The complete phase separation was achieved for time longer than 10 min. A centrifugal time of 15 min was chosen as the best condition.

3.6. Calibration, precision and detection limits

Calibration graphs were obtained by the preconcentrating 100 ml of a sample in the presence of 0.12% (w/v) Triton X-114 under the optimum experimental conditions. Calibration parameter, standard deviation obtained for 10 analyte samples subjected to the complete procedure and the detection limits as shown in Table 4.

The preconcentration factor calculated as the ratio of the concentration of analyte after preconcentration to that prior to preconcentration, which gives the high absorbance peak area (50-fold). The precision of the method was established by repeated assays ($n = 10$) using $10 \mu\text{g l}^{-1}$ solution of nickel. The standard deviation ranges from 0.013 to 0.154% for nickel. The limit of detection was satisfactory and found to be 0.042 ng ml^{-1} . In this case, preconcentration of only 100 ml of sample in the presence of 0.12% (w/v) Triton X-114 permitted the detection of 0.042 ng ml^{-1} .

Table 2
Recovery of nickel from various concentrations of spiked water samples using preconcentration cloud-point extraction

| | Proposed method | Reported method [33] |
|--|-----------------|----------------------|
| Concentration of nickel added (ng l^{-1}) | | |
| 20 | | |
| Found (ng l^{-1}) | 19.81 | 19.78 |
| Recovery (%) | 99.05 | 98.90 |
| S.D. ^a (%) | ± 0.065 | ± 0.64 |
| <i>t</i> - and <i>f</i> -test | 0.101, 0.192 | |
| 40 | | |
| Found (ng l^{-1}) | 39.85 | 39.72 |
| Recovery (%) | 99.62 | 99.30 |
| S.D. ^a (%) | ± 0.168 | ± 0.11 |
| <i>t</i> - and <i>f</i> -test | 0.431, 0.219 | |
| 60 | | |
| Found (ng l^{-1}) | 59.66 | 59.78 |
| Recovery (%) | 99.86 | 99.63 |
| S.D. ^a (%) | ± 0.068 | ± 0.09 |
| <i>t</i> - and <i>f</i> -test | 0.285, 0.402 | |
| 80 | | |
| Found (ng l^{-1}) | 79.88 | 79.91 |
| Recovery (%) | 99.93 | 99.88 |
| S.D. ^a (%) | ± 0.454 | ± 0.14 |
| <i>t</i> - and <i>f</i> -test | 0.337, 0.014 | |

^a Recovery (%) and S.D. for 10 determinations.

3.7. Effect of non-target species

The influence of matrix ions in various water samples on the recovery of nickel ions was also investigated. It indicates that Co^{2+} , Cu^{2+} ($50 \mu\text{g ml}^{-1}$), Cr^{3+} , Cu^{2+} ($10 \mu\text{g ml}^{-1}$), Mn^{2+} , Mn^{2+} ($200 \mu\text{g ml}^{-1}$), Ca^{2+} ($400 \mu\text{g ml}^{-1}$), IO_3^- , Br^- , SO_4^{2-} , Cd^{2+} , Zn^{2+} , Pb^{2+} ($800 \mu\text{g ml}^{-1}$) and Na^+ , K^+ , CS^+ , NO_3^- , PO_4^{3-} , Cl^- , Br^- , I^- ($1000 \mu\text{g ml}^{-1}$), in any do not interference in ordinary condition during the present study.

3.8. Application of the present method and statistical comparison with reported method

The data obtained with the proposed method for the preconcentration and cloud-point extraction of nickel employed for the spiked and natural water samples were presented in Tables 2 and 3. The proposed method for the determination of

Table 3
Determination of nickel using cloud-point extraction from natural water samples collected in and around Tirupati area

| Sample | Nickel found (ng ml^{-1}) ^a ($n = 10$) | |
|------------------------|--|----------------------|
| | Proposed method | Reported method [33] |
| Sample-I | 12.18 ± 0.013 | – |
| Sample-II | 21.05 ± 0.05 | – |
| Narsingapuram | 9.73 ± 0.02 | – |
| Swarnamukhi river belt | 10.67 ± 0.03 | 10.69 ± 0.8 |
| Kalyanidam reservoir | 17.16 ± 0.09 | 17.20 ± 0.5 |
| Ghajulamandyam area | 25.31 ± 0.04 | 25.32 ± 0.8 |

^a For 10 determination.

Table 4
Analytical characteristics of the present method

| Parameters | Analytical feature |
|--|-------------------------------------|
| Preconcentration factor ^a | 50 |
| S.D. (%) ^b | 0.013 |
| Regression equation, C ($\mu\text{g l}^{-1}$) | $Y = 11.05 \times 10^{-3}C + 0.015$ |
| Correlation co-efficient (r) | 0.9997 |
| Linear range ($\mu\text{g l}^{-1}$) ^c | 0.10–1.18 |
| Limit of detection (ng ml^{-1}) | 0.042 |

^a Ratio of the concentration of analyte without the application of CPE technique to that after the CPE, giving the same analytical response.

^b $n = 10$.

^c For spiked concentration (0.12%, w/v).

Nickel using cloud-point extraction has been employed for real samples of water were presented in Table 3. The obtained result (natural water samples) was compared with the reported method [33]. The analytical data summarized in Table 2 (spiked water samples) suggest that the percentage of nickel recovery from water samples ranges from 99.05 to 99.93%, which is more reliable and sensitive than the other methods. For the validation of the proposed method, a certified material (SPS-SW2/ $\mu\text{g l}^{-1}$) was analyzed and the analytical result $48.18 \pm 0.6 \mu\text{g l}^{-1}$ is in good agreement with certified value of $50.0 \pm 0.3 \mu\text{g l}^{-1}$ (Table 4).

Present method was compared with the reported methods in the literature in terms of detection limits and instruments employed for the analysis of metal ions in various environmental samples. It is evident from the above data that the proposed method is facile, rapid and more sensitive (Table 5).

Table 5
Comparison of the present method with reported methods for the preconcentration and CPE of nickel

| Reagent | Surfactant | Technique | Detection limit | References |
|--|--------------|-----------|--------------------|------------|
| 1-(2-Thiazolylazo)-2-naphthol | Triton X-114 | FAAS | 0.24 ^a | [16] |
| 1-(2-Pyridylazo)-2-naphthol | Triton X-114 | FAAS | 0.38 ^a | [34] |
| 1-Nitroso-2-naphthol | PONPE 7.5 | FAAS | 1.22 ^b | [35] |
| <i>N</i> -benzoyl- <i>N</i> -phenyl hydroxylamine | Triton X-114 | FAAS | 2.08 ^a | [36] |
| 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone | Triton X-100 | FAAS | 0.64 ^a | [37] |
| <i>N</i> -quino[8,7- <i>b</i>]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[<i>b</i>][1,4,7,10,13]pentaoxacyclopentadecin-15-yl-methanimine | Triton X-114 | FAAS | 0.042 ^a | This work |

^a ng ml^{-1} .

^b $\mu\text{g ml}^{-1}$.

4. Conclusions

Cloud-point extraction offers a simple, rapid, economical and eco-friendly methodology for preconcentration and separation of nickel in various water samples prior to their analysis by flame atomic absorption spectrometry (FAAS). The present method has added advantages over reported methods (Table 5):

- (1) Synthesis of metal chelating agent *N*-quino[8,7-*b*]azin-5-yl-2,3,5,6,8,9,11,12octahydrobenzo[*b*][1,4,7,10,13]pentaoxa-cyclopentadecin-15-yl-methanimine at ordinary laboratories was simple and economical.
- (2) Synthesized organic reagent is distinct in terms of sensitivity, selectivity towards metal ions.
- (3) Optimum volume of the surfactant-rich phase obtained by using the present cloud-point methodology permitted to design an extraction strategy presenting robustness, low cost, good extraction efficiency and lower toxicity than those using organic solvents.
- (4) The proposed method gives very low detection limits and good S.D.s and can be applied to the determination of traces of nickel in various water samples.

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