Solid Phase Extraction of Ultra Trace Amounts of Ni^{2+} by Dimethylglyoxime (DMG) Immobilized on Column

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ABSTRACT: *A column of alumina modified with sodium dodecyl sulfate (SDS) and dimethylglyoxime (DMG) was prepared for the preconcentration of trace nickel from water samples for flame atomic absorption spectrometry (FAAS) determinations. Under optimized conditions (pH=7.0; flow rate: 20 mlmin^{-1}) nickel was retained on the column. The nickel collected on the column was eluted with 5 mL of 1 M nitric acid. Recovery was greater than 98%. A concentration factor of 200 can be achieved by passing 1000mL of sample through the column. The relative standard deviation (10 replicate analyses) at the 200 ngml^{-1} level for nickel was 2.2% and the corresponding limit of detection (based on 3σ) was 0.82 ngml^{-1}. The method was applied to the determination of nickel in row solution for nickel plating.*

KEY WORDS: *Nickel determination, Atomic absorption spectrometry, Surfactant, Dimetylglyoxim.*

INTRODUCTION

Analytical separation techniques play a central role in today's analytical chemistry. They are typically used to enrich one of the sample fractions contacting a given component in trace analysis, as well as, to remove complex matrix for enhanced sensitivity or selectivity, respectively, in ordinary analytical methods. The preconcentration technique has been used to improve the sensitivity and selectivity of trace analyses by replacing the original sample matrix with a new, non-interfering one. The enrichment technique has often been used to collect trace elements on solid surfaces [1].

Solid phase extraction (SPE) is a preconcentration technique of rapidly growing importance in trace metal determinations with atomic absorption spectrometry [2].

SPE has a number of attractive features compared with the traditional extraction techniques. It is fairly simple, inexpensive, can be used in the field, needs relatively little toxic solvents, and can be easily automated [3].

Many methods have been developed for preconcentration of trace metals from natural waters. These include coprecipitation, electrodeposition, liquid-liquid extraction, ion exchange technique, filtration and sorption. Adsorption of complexed metals on various sorbents, such as activated carbon (AC)[4], Amberlite XAD[5], silica gel[6] and other sorbents[7], have been widely applied to preconcentration of metals from water samples.

Electrothermal atomic absorption spectrometry (ETAAS) has been used for direct determination of trace

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amounts of nickel in several water samples. But often preconcentration procedure for Ni determination even with ETAAS detection are necessary [8].

Another method for SPE preconcentration is activated sorbent by surfactant and hydrophobic chelating agent [9]. Also water insoluble chelating agent were introduced into the hemimicelles of SDS coated alumina for preconcentration of trace elements.

Surfactant molecules form self-aggregate structures called "critical micellar concentration "(CMC). The formation of micelles is aided by cooperative interaction (due to van der waals forces) between the long hydrocarbon chains of surfactant molecules. Similar surfactant aggregate can be formed on solid surfaces such as silica [10] calys [11], ferrihydrite [12], Amberlite XAD-2 resin [13] and alumina [14-16]. They are called "hemimicelles" or "admicelles" and interior tend to incorporate sparingly soluble organic substances. Recent developments in preconcentration separation and determination of nickel[17-24] are summarized in Table1.

α –Dioximes are widely used as selective precipitating detecting and photometric reagent for Ni , Pd(II) and some other metal ions . DMG has also been used for the spectrophotometric determination of nickel[25].

In the work presented here, a rapid, highly sensitive and efficient method for determination of trace nickel in natural water sample by FAAS, using a column packed with alumina modified with SDS and DMG for the selective extraction and concentration was applied. The system was evaluated for the determination of nickel in raw solution for nickel plating.

EXPERIMENTAL

Reagents

Analytical reagent-grade chemicals and doubly distilled de-ionized water were used. All glassware was soaked in 5%(v/v) nitric acid for at least 24 h and washed with water.

Alumina powder: γ-alumina (particle size, 10-50μm; chromatographic grade; Darmstadt, Germany) was purified prior to use by shaking with 4moll^{-1} nitric acid, and washing three times with water.

Sodium dodecyl sulfate (SDS): the analytical-grade reagent (Schuchardt; Germany) was used without further purification.

Dimetylglyoxime Solution: the reagent solution was prepared by dissolving 0.1g of DMG [dimetylglyoxime] in 100 ml of 95% ethanol.

Stock solution of 1000 μgml^{-1} of Ni was prepared by dissolving Ni(NO3)2, 6H2O (Merck) in concentrated nitric acid and diluting to 100 ml with water . Working solutions were prepared from the stock solution by serial dilutions with distilled water.

Apparatus

A Metrohm 713 pH meter was used for measuring the pH of the solutions. A Varian 220 (Varian,Spain) Model AA-1475 atomic absorption spectrometer equipped with deuterium correction and nickel hollow-cathode lamp as the radiation source was used .All absorption measurements were performed under the following operation conditions: wave-length: 232 nm; band pass: 0.5 nm; current: 15 mA and using an air- acetylene flame.

Table 1:Comparison of published method for the determination of nickel by separation techniques

No	Technique	Sorbent	DL (μg/l)*	Ref
1	FAAS	XAD-2 (BTAC)	1.1	17
2	UV	Naphthalene	10	18
3	ICP-AES	XAD-2 (PAN)	16	19
4	FI-UV	PUF	77	20
5	UV	Naphthalene	300	21
6	FI-ETAAS	C-60	0.075	22
7	Voltammetry	Carbon paste (DMG)	0.7	23
8	ETAAS	----------	32.1(μg/Kg)	24

** Detection limit*

Preparation of the column

Purified alumina particles (6 g) were suspended in 200 ml of water and mixed with 0.4 g of SDS and suspension was acidified to pH 2-2.5 with 4 $moll^{-1}$ hydrochloric acid and mixed for 15 min with a mechanical shaker. Then added 8 ml DMG solution (0.1%w/v) and was adjusted to pH 8-9 and mixed for 15 min with a mechanical shaker again. After the supernatant solution was discarded, the DMG-coated alumina was packed into a column (23 mm× 30 mm i.d.).

Recommended procedure

20 ml of water was adjusted to pH=10 and passed through the column. Then a given volume of aqueous sample up to 1000 ml Ni^{2+}, after adjustment to pH 7.0 with 4 $moll^{-1}$ hydrochloric acid, was passed through the column at a flow rate of 20 $mlmin^{-1}$. The adsorbed metal was eluted with 5 ml of 1 $moll^{-1}$ nitric acid at an elution rate of 2 $mlmin^{-1}$. The nickel ion concentration in eluate was determined by FAAS.

RESULTS AND DISCUSSION

Immobilization of DMG on alumina

The anionic surfactant, SDS, is effectively sorbed on the positively charged alumina surface to form aggregates [26], therefore negatively charged SDS surfactant ions are adsorbed at low pH values due to increased interaction between the alumina and SDS [27]. Nearly complete adsorption was achieved at pH 1- 4 by shaking for 15 min.

We thus, tried to coat alumina surfaces with SDS into which DMG could be subsequently trapped. We mixed DMG and 6 g alumina and 0.4 g SDS as described in experimental. SDS would form hemimicelles or admicelles on alumina by strong adsorption and the micelles could trap DMG molecules, homogeneously.

Effect of pH

The effect of the pH of solutions containing of Ni^{2+} was examined in the pH range 1-12 and the percentage retention of metal cation on the adsorbent was calculated. The results are shown in Fig.1. Nickel cation was adsorbed quantitatively at the pH range 6-9.The decrease in binding at lower pH values was attributed to the protonation of weakly basic coordination group of ligand and the decrease in binding at higher pH values was attributed to the effect of masking of OH^- for Ni^{2+}.

Effect of flow rate

The effect of flow rate of the solution through the column on the retention behavior of Ni^{2+} was studied over the range 1-50 $mlmin^{-1}$.

Adsorption begins to decrease with an increase in the flow rate when the latter is greater than 25 $mlmin^{-1}$. The metal is adsorbed quantitatively at a flow rate of 20 $mlmin^{-1}$ and subsequently eluted with 1 M nitric acid at an elution rate of 2 $mlmin^{-1}$.

Effect of sample volume

The effect of changes in the volume of sample solution passed through the column packed with DMG-coated alumina, on the adsorption of Ni^{2+} was examined (Table 2). No decline in the percentage adsorption of Ni^{2+} was observed up to a volume of 1000 ml, the maximum tested in these experiments. In the present work as the elution volume is 5 ml the preconcentration factor is obtained up to 200.

Capacity of the sorbent

In order to study the adsorptive capacity of DMG-coated alumina for nickel cation batch method was used. To 6 g DMG-coated alumina was added 50 ml of solution containing 10 mg of nickel at pH 7. After shaking for 1 h, the mixture was filtered. The supernatant solution was diluted and determined by flame atomic absorption spectrometry. The capacity of sorbent was found 2.43 mgg^{-1}.

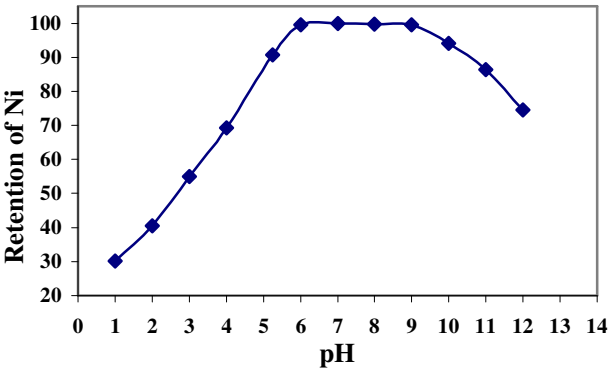

Fig. 1: Effect of pH on the adsorption of nickel on DMG – coated alumina. Concentration of standard solution Ni^{2+} 200 ng ml^{-1}, flow rate : 20 ml min^{-1} , initial volume : 50 ml, final volume : 5 ml.

Interference effects

The reliability of the proposed method was examined in the natural water samples. The tolerance limits in μgml^{-1} of coexisting ions, set as the largest amount yielding a change of less than 3% in the adsorption efficiency of 200 ng ml^{-1} of nickel, are as follows: Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{6+}, Na^{+}, Cs^{+}, F^{-}, Cl^{-}, I^{-}, NO^{3-}, VO^{3-} (1000); CH_3COO^{-} (800); Pd^{2+} (250); Mn^{2+} (200); Fe^{2+} (150); Cr^{3+}, Cu^{2+} (100); Co^{2+}, Zn^{2+} (40).

Precision and detection limit

The relative standard deviation (10 replicate analyses) at 200 $ngml^{-1}$ for nickel cation was 2.2 % and corresponding of detection (based on 3σ) was 0.82 $ngml^{-1}$.

Application to samples

The method was applied to the determination of nickel cation in row solution for nickel coating, mineral water and Karaj River water. The average percent recoveries obtained for the addition of Ni^{2+} spikes to water samples are given in Table 3.

Conclusions

A method using a column of alumina loaded with DMG combined with FAAS has been developed and tested for the preconcentration of nickel from a large volume of the aqueous solution for nickel using AAS. Using a selective ligand such as DMG in a selective and sensitive technique such as AAS yielded a selective and sensitive analytical method.

The preconcentration method provided is simple, sensitive, accurate with a low detection limit for separation and determination nickel cation from dilute solutions. Concentrations as low as $ngml^{-1}$ can easily be determined, and precise results are obtained. The detection limits found with this method (0.82 $ngml^{-1}$) are very satisfactory owing to the enhanced sensitivity achieved via preconcentration.

In conclusion, flame atomic absorption spectrometry using alumina could be used in water analyses provided one does it with appropriate care.

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Table 2:Effect of volume of sample solution on the adsorption of Ni2+

Ni added,μg	20	20	20	20	20
Sample passed,ml	50	100	250	500	1000
Recovery, %	99.4	98.7	98.6	99.1	98.1
Concentration factor	10	20	50	150	200

Amount of Nickel: 20 μg , pH : 7, flow rate of sample : 20 ml min^{-1}.

Table 3 : Recovery of nickel spikes from row solution for nickel plating and natural waters.

Sample	Nickel ($ngml^{-1}$)	Concentration Recovery*($ngml^{-1}$)	RSD%
Row Solution	0.0	21.8	2.8
	10.0	32.0	1.5
	20.0	41.9	2.6
Mineral water	0.0	5.1	3.1
	10.0	14.9	2.6
	20.0	24.9	2.5
Karaj River	0.0	48.3	2.3
	10.0	58.1	2.7
	20.0	68.2	2.6

Sample volume:500 ml, eluent volume : 5ml,
pH:7, flow rate of sample: 20 ml min^{-1}.
**Average and standard deviation of three determinations*

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