Study on Solid Phase Extraction and Spectrophotometric Determination of Nickel in Waters and Biological Samples

Qiufen Hu,[†,‡] Guangyu Yang,[†,*] Zhangjie Huang,[†] and Jiayuan Yin[†]

[†]*Department of Chemistry, Yunnan University, Kunming, 650091, P.R. China*
[‡]*Department of Chemistry, Yuxi Teachers College, Yuxi, 653100, P.R. China*
Received April 25, 2003

A sensitive, selective and rapid method for the determination of nickel based on the rapid reaction of nickel(II) with QADMAA and the solid phase extraction of the Ni(II)-QADMAA chelate with C_{18} membrane disks has been developed. In the presence of pH 6.0 buffer solution and sodium dodecyl sulfonate (SDS) medium, QADMAA reacts with nickel to form a violet complex of a molar ratio of 1 : 2 (nickel to QADMAA). This chelate was enriched by solid phase extraction with C_{18} membrane disks. An enrichment factor of 50 was obtained by elution of the chelates form the disks with the minimal amount of isopentyl alcohol. The molar absorptivity of the chelate was 1.32×10^5 L mol^{-1} cm^{-1} at 590 nm in the measured solution. Beer's law was obeyed in the range of 0.01-0.6 μg/mL. This method was applied to the determination of nickel in water and biological samples with good results.

Key Words : 2-(2-Quinolylazo)-5-dimethylaminoaniline, Nickel, Spectrophotometry, Solid phase extraction

Introduction

Nickel is an important element, not only for industry, but for biological systems as well.[1,2] Many sensitive instrumental methods, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence, have widely been applied to the determination of nickel.[3-8] However, the spectrophotometric method still has the advantages of simplicity and of not requiring expensive or complicated test equipment. This has led to the development of a wide variety of spectrophotometric methods for the determination of nickel.[9-16]

In previous work, we reported some 2-quinolylazo-phenol reagents for the determination of metal ions.[16-21] This kind of reagent, because of its larger conjugated system, has a higher sensitivity than pyridylazo reagents. However, the 2-quinolylazo-phenol reagent has also the disadvantage of its poor selectivity because both the oxygen atoms and nitrogen atoms donate to the metal ions. To select a more sensitive and selective reagent, we synthesized 2-(2-quinolinylazo)-5-dimethylaminoaniline (QADMAA) and thoroughly studied the color reaction of QADMAA with nickel. This reagent has higher selectivity than 2-quinolylazo-phenol reagents because it only donates nitrogen atoms to metal ions.

Routine spectrophotometric methods are often not sensitive enough to determine low concentrations of nickel ion in environmental samples, *i.e.* nickel concentrations less than the μg/L level. Consequently, a preconcentration step is usually required. Solid phase extraction is an attractive technique because of its notable advantages.[22-26] The present paper, based on the color reaction of QADMAA with nickel and the solid phase extraction of the colored chelate with C_{18} disks, describes the development of a highly sensitive, selective and rapid method for the determination of nickel in water and biological samples.

[*]Corresponding Author. Fax: +86-871-8316812; e-mail: huqiufena @163.com

Experimental Section

Experimental Apparatus. A UV-160A spectrophotometer (Shimidzu, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ-200 pH meter. The extraction was performed on Waters Solid Phase Extraction (SPE) Device (It can prepare twenty samples simultaneously), and Zorbax C_{18} membrane disks [47 mm (diameter) $\times$ 0.5 mm (thickness), 8 μm, 50 mg] (Agilent Technologies, USA) were used.

Reagents. *Synthesis of QADMAA:* 2-aminoquinoline (6.9 g) was dissolved in 500 mL of anhydrous ethanol. To which, sodamide (2.0 g) was added, and the mixture was refluxed in a boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL). The solution was refluxed for 30 min in a boiling water bath. The solution was cooled and stored over night at under 0 ^{o}C. The diazo salt was obtained by filtering this solution with an isolation yield of 95%. The diazo salt was dissolved in 200 mL anhydrous ethanol, followed by the addition of *m*-dimethylaminoaniline (5.7 g; 0.042 mol). The carbon dioxide was ventilated into the solution with stirring until the pH reached about 8.0. The solution was let stand for two days, evaporating to dryness. The residue was re-crystallized with 30% ethanol. QADMAA was obtained with 36% yield. The structure of QADMAA was verified by elemental analysis, IR (Fig. 1), ^{1}H NMR (Fig. 2), and MS (Fig. 3). Elemental analysis: $C_{17}H_{17}N_5$ found (calculated) C 69.82 (70.08), N 23.83 (24.04), H 6.04 (5.88). All these data show that the QADMAA has the structure in Figure 4.

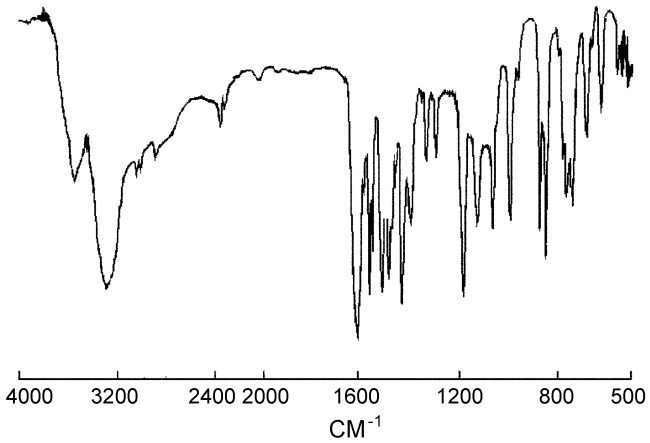

Figure 1. The infrared spectrum of QADMAA.

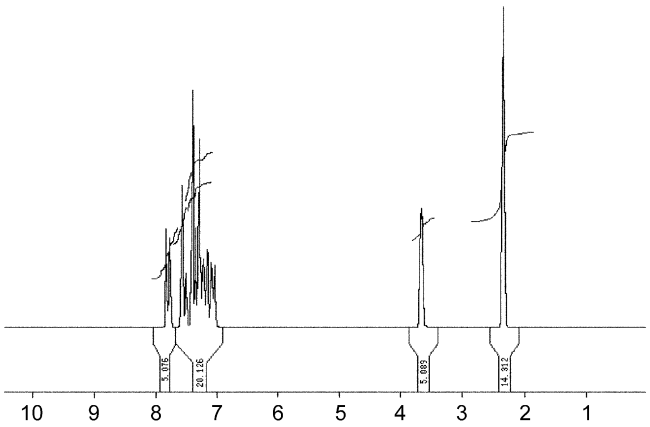

Figure 2. The 1H nuclear magnetic resonance spectrum of QADMAA.

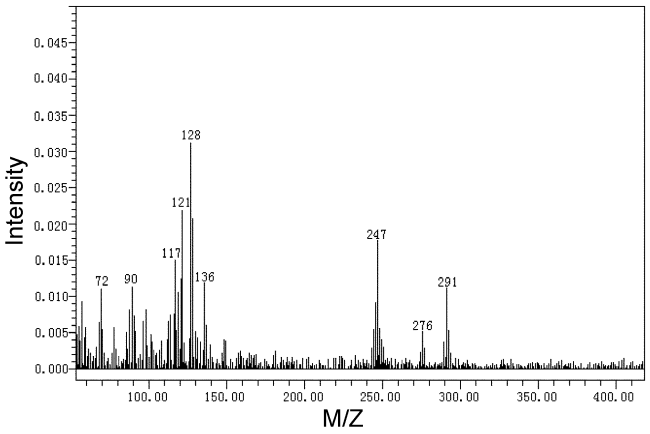

Figure 3. The mass spectrum of QADMAA.

All the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). High purity isopentyl alcohol (Fisher Corporation, USA) was used. A 5×10^{-4} mol/L of QADMAA solution was prepared by dissolving QADMAA with 95% of ethanol. A stock standard solution of nickel (1.0 mg/mL) was obtained from the Chinese Standard Center, and a work solution of 1.0 μg/mL was prepared by diluting

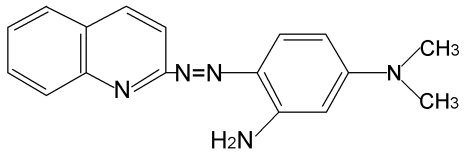

Figure 4. The structure of QADMAA.

this solution. A hexamine-hydrochloric acid buffer solution, 0.5 mol/L with a pH = 6.0 containing 0.1 mol/L sodium thiosulfate and 0.2 mol/L sodium fluoride), was used. Sodium dodecyl sulfonate (SDS) solution (1.0% (m/v)) was prepared by dissolving SDS with water. All chemicals used were of analytical grade unless otherwise stated.

General procedure. To a standard or sample solution containing no more than 2.4 μg of Ni(II) in a 200 mL calibrated flask, 10 mL of 0.5 mol/L hexamine-hydrochloric acid buffer solution (containing 0.1 mol/L sodium thiosulfate and 0.2 mol/L sodium fluoride) with pH 6.0, 6 mL of 5×10^{-4} mol/L QADMAA solution and 5.0 mL of 1.0% SDS solution were added. The mixture was diluted to 200 mL and mixed well. After 10 min, the solution was passed through the C_{18} disks at a flow rate of 50 mL/min. After the enrichment, the retained chelates were eluted from the disks with 4 mL of isopentyl alcohol at a flow rate of 5 mL/min, and the eluent was adjusted to the accurate volume of 4.0 mL in a 4.0 mL calibrated flask by adding microamount of isopentyl alcohol with a 500 μL syringes. The absorbance of the eluent was measured in a 1 cm cell at 590 nm against a reagent blank prepared in a similar way without nickel.

Results and Discussion

Absorption Spectra. The absorption spectra of QADMAA and its Ni(II) complex in isopentyl alcohol medium are shown in Figure 5. The absorption peaks of QADMAA and its complex are located at 454 nm and 590 nm.

Effect of Acidity. Results show that the optimal pH for the

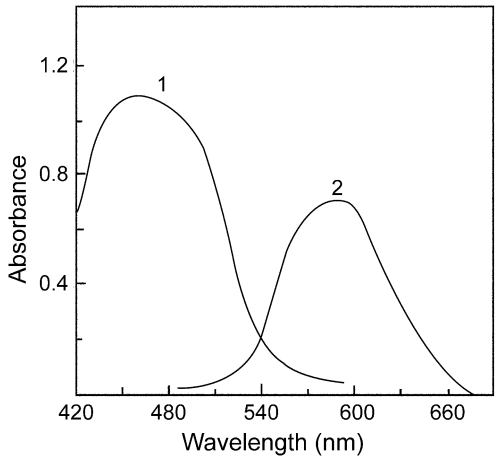

Figure 5. Absorption spectra of QADMAA and its Ni(II) complex in isopentyl alcohol medium: 1, QADMAA-SDS blank against water; 2, QADMAA-Ni(II)-SDS complex against reagent blank. The concentration of Ni(II) is 4.16×10^{-6} mol/L, QADMAA is 3.22×10^{-4} mol/L, other conditions as general procedure.

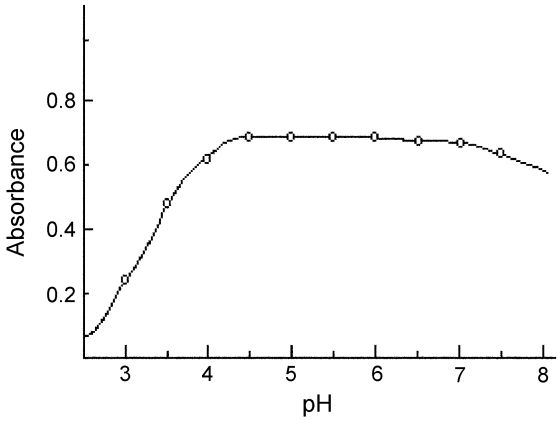

Figure 6. Effect of pH on the formation of Ni(II) complex, Ni(II) concentration was 5.0×10^{-6} mol.l^{-1}, other conditions as general procedure.

reaction of Ni(II) with QADMAA is 4.8-8.2 (Fig. 6). An hexamine-hydrochloric acid buffer solution of pH 6.0 is recommended to control pH, as the use of 8-15 mL buffer solution (pH 6.0) per 200 mL of final solution was found to give a maximum and constant absorbance. The use of 10 mL of buffer solution is recommended. The buffer solution containing a 0.08-0.15 mol/L of sodium thiosulfate and 0.15-0.25 mol/L of sodium fluoride can increase the selectivity of this system [Without sodium thiosulfate and sodium fluoride in the buffer solution, the tolerance limits of foreign ions were 0.002 mg for Cu(II), Zn(II); 0.005 mg for Ag(I), Fe(III), Pd (II). However, the tolerance limits of foreign ions reached 1.0 mg for Fe(III); 0.1 mg for Cu(II), Zn(II); 0.05 mg for Pd(II), Ag(I) when sodium thiosulfate and sodium fluoride existed in the buffer solution]. So 0.1 mol/L of sodium thiosulfate and 0.2 mol/L of sodium fluoride in buffer are recommended.

Effect of Surfactants. The effect of surfactants on the Ni(II)-QADMAA chromogenic system is studied (Table 1). In the absence of surfactants, as well as cationic surfactants (cetyltrimethylammonium bromide (CTMAB)) or cetylpyridinium bromide (CPB)) medium, the Ni(II)-QADMAA chromogenic system gives a low absorption, whereas in the presence of anionic surfactants or nonionic surfactants medium, the absorption of the chromogenic system increases markedly. Experiments show that SDS is the best additive. The use 4-8 mL of SDS solution gives a constant and maximum absorbance. Accordingly, the use of 5 mL is recommended.

Effect of QADMAA Concentration. For up to 2.4 μg of Ni(II), the use of about 5-10 mL of 5×10^{-4} mol/L QADMAA solution has been found to be sufficient for a complete reaction. Accordingly, 6 mL of QADMAA solution were added in all further measurements.

Stability of the Chromogenic System. After mixing the components, the absorbance reached its maximum within 6 min at room temperature and remained stable for 6 h in aqueous solution. The chelates were stable at least 20 h, after which they were extracted into the isopentyl alcohol medium.

Solid Phase Extraction. Both the enrichment and the elution were carried out on a Waters SPE device (which can prepare twenty samples simultaneously). The flow rate was set to 50 mL/min for enrichment and 5 mL/min for elution.

Some experiments were carried out to investigate the retention of QADMAA and its Ni(II) chelate on the disks. We found that the QADMAA and its Ni(II) chelate can be retained on the disks quantitatively when they pass the disks as aqueous solution. The capacity of the disks for QADMAA was 36 mg and for its Ni(II)-chelate 31 mg in a 200 mL of solution. In this experiment, the disks have adequate capacity to enrich the Ni(II)-QADMAA chelate and the excessive QADMAA.

In choosing the proper eluent to retained QADMAA and its Ni(II) chelate, various organic solvents were studied. The effect of various organic solvents was in the following sequence: isopentyl alcohol > acetonitrile > acetone > ethanol > methanol. So isopentyl alcohol was selected as the eluent. Our experiment shows that it is easier to elute the retained QAMAA and its Ni(II) chelate in reverse direction than in forward direction, so it is necessary to upturned the disks for the elution. 4.0 mL of isopentyl alcohol was a sufficient amount to elute the QADMAA and its Ni(II) chelate from disks at a flow rate of 5 mL/min. The volume of 4.0 mL eluent was selected.

Table 2. Tolerance limits for the determination of 2 μg of Ni(II) with QADMAA (relative error ± 5%)

Ion added	Tolerate (mg)
NO_3^-, K^+, borate, Mg^{2+}	50
Li^+, Al^{3+}, PO_4^{3-}, NO_2^-, SO_4^{2-}, ClO_4^-	5
Ca^{2+}, Sr^{2+}, IO_3^-, BrO_3^-, B(III), ClO_3^-	2
Mn^{2+}, Ce(IV) , Fe^{3+}, Mo(VI), Br^-	1
Ti(IV), Bi(III), V(V), Cr(VI), Cr(VI), Ba^{2+} W(WI), U(IV)	0.3
Cd^{2+}, Pd^{2+}, Cr^{3+}, La^{3+}, Cl^-, Zn^{2+}, Cu^{2+}, Zr(IV)	0.1
Bi(III), Pb^{2+}, Hg^{2+}, Sb^{3+}, Th(IV), Ag^+, Sn(IV), Pd^{2+}	0.05
Se(IV), Te(IV), Au^{3+}	0.03
Co^{2+}	0.02

Table 1. The effect of surfactants on Ni(II)-QADMAA chromogenic system

Surfactant	Absence	CTMAB	CPB	TritonX-100	Tween-80	Tween-20	SDS	SDBS	SLS
λ_{max} (nm)	580	580	580	590	585	580	590	588	590
ε ($\times 10^4$) l.mol^{-1}.cm^{-1}	7.94	6.86	7.21	9.47	9.36	8.23	13.2	10.6	11.2

SDS (Sodium dodecyl sulfonate), SDBS (Sodium dodecyl benzenesulfonate), SLS (Sodium lauryl sulfate)

Table 3. Determination of nickel in the certified standard biological samples

Samples	Standard value (μg/g)	By this method (μg/g)	RSD % (n=5)
Human hair (GBW07601)	As(0.28), B(1.3), Bi(0.34), Ca(2900), Cd(0.11), Ce(1.2), Co(0.71), Cr(0.37), Cu(10.2), Fe(54), Hg(0.36), Mg(360), Mn(6.3), Mo(0.073), Ni(0.83), Pb(8.8)	0.846	2.8
Tea Leaf (GBW08505)	As(0.191), Ba(15.7), Ca(2840), Cd(0.032), Co(0.2), Cr(0.8), Cu(16.2), Fe(373), Hg(0.004), Mg(2240), Mn(766), Ni(7.61), Pb(1.06), Se(0.041), Zn(38.7)	7.59	2.4

Table 4. Determination of Nickel in the water sample

Samples	Reference method (μg/L)	Found * (μg/L)	RSD % (n=5)	Recovery (%) (n=5) (Add 1.0 μg nickel)
River water	46.7	48.2	2.5	96
Lake water	22.8	23.2	2.4	104
Tap water	14.9	15.6	2.7	97

Calibration Curve and Sensitivity. The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01-0.6 μg Ni(II) per mL. The linear regression equation obtained was: $A = 2.326\ C$ (μg/mL) + 0.0125, ($r = 0.9994$). The molar absorptivity was calculated to be 1.32×10^5 L mol^{-1} cm^{-1} at 590 nm. The relative standard deviation at a concentration level of 0.2 μg Ni(II) per mL (11 repeat determination) was 1.29%.

Composition of the Complex. The composition of the complex was determined by continuous variation and molar ratio method. Both showed that the molar ratio of Ni(II) to QADMAA is 1 : 2.

Interference. The selectivity of the proposed method was investigated by the determination 2.0 μg/200 mL of Ni(II) in the presence of various ions within a relative error of ± 5%. See Table 2.

Application. The proposed method has been successfully applied to the determination of nickel in biological samples and water samples.

For biological samples, an accurately weighed 0.20 g sample was placed in the Teflon high-pressure microwave acid digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). 2.5 mL of concentrated nitric acid and 2.5 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 1% of hydrochloric acid, and the nickel contents were analyzed according to general procedures. The results are shown in Table 3.

For water samples, the samples were acidified with hydrochloric acid and filtered with a 0.45 μm filter. The nickel contents were analyzed according to general procedure. The results are shown in Table 4, together with the results of a recovery test. A standard method using ICP-MS has been used as a reference method. The results are also shown in Table 4.

Acknowledgement. This project was supported by the Natural Science Foundation of Yunnan Province (0111143).

References

1. Denkhaus, E. ; Salnikow, K. *Critical Reviews in Oncology* **2002**, *42*(1), 1040-8428.
2. Baldan, A. *Journal of Materials Science* **2002**, *37*(11), 2171-2202.
3. Ming, H.; Zhang, Y. L. *Journal of Trace and Microprobe Techniques* **2002**, *20*, 1-14.
4. Benzo, Z.; Marcano, E.; Gomez, C.; Ruiz, F.; Salas, J.; Quintal, M.; Garaboto, A. *Journal of AOAC International* **2002**, *85*(4), 1060-3271.
5. Sreenivasa, K.; Balaji, T.; Prasada, T. *Spectrochimica Acta, Part B (Atomic Spectroscopy)* **2002**, *57B*, 1333-1338.
6. Zendelovska, D.; Pavlovska, G.; Cundeva, K.; Stafilov, T. *Talanta* **2001**, *54*, 139-146.
7. Natalija, I.; Ershova, V.; Ivanov, M. *Fresenius' Journal of Analytical Chemistry* **2000**, *367*, 210-211.
8. Hu, Q. F.; Yang, G. Y.; Yin, J. Y. *Analytical and Bioanalytical Chemistry* **2003**, *375*, 831-835.
9. Fan, X. Z.; Zhu, C. H.; Zhang, G. F. *The Analyst* **1998**, *123*, 109-112.
10. Hu, Q. F.; Yang, G. Y.; Huang, Z. J.; Yin, J. Y. *Analytical Sciences* **2003**, *19*(10), 1158-1161.
11. Ma, Q. L.; Su, M. H.; Wang, Z. H.; Nie, L. H.; Liang, S. C.; Ma, H. M. *Analytica Chimica Acta* **2001**, *439*, 73-79.
12. Lucia, H. S.; Avila, T. M. C.; Cunha, A. I. *Spectroscopy Letters* **1999**, *32*, 257-271.
13. Fan, X. Z.; Zhu, C. H. *Microchemical Journal* **1998**, *59*, 284-293.
14. Hu, Q. F.; Yang, G. Y.; Tang, D. Y.; Yin, J. Y. *Fenxi Huaxu* **2002**, *30*, 699-701.
15. Zhao, S. L.; Xia, X. Q.; Ma, H. R.; Xi, H. J. *Talanta* **1994**, *41*, 1353-1356.
16. Ishizuki, T.; Tsuzuki, M.; Yuchi, A.; Ozawa, T.; Wada, H.; Nakagawa, G. *Analytica Chimica Acta* **1993**, *272*, 161-167.
17. Hu, Q. F.; Yang, G. Y.; Yang, J. H.; Yin, J. Y. *Journal of Environment Monitoring* **2002**, *4*(6), 956-959.
18. Yang, G. Y.; Hu, Q. F.; Huang, Z. J.; Yin, J. Y. *Analytical Sciences* **2003**, *19*, 299-302.
19. Simgh, I.; Poonam, M. *Talanta* **1984**, *31*, 109-112.
20. Li, Z.; Yang, G. Y.; Wang, B. X.; Jiang, C. Q.; Yin, J. Y. *Journal of Chromatography A* **2002**, *971*, 243-248.
21. Yang, G. Y.; Hu, Q. F.; Huang, Z. J.; Yin, J. Y. *Analytical and Bioanalytical Chemistry* **2002**, *374*, 1325-1329.
22. Garg, B. S.; Sharma, R. K.; Bhojak, N.; Mittal, S. *Microchem. J.* **1999**, *61*, 94-102.
23. Pyrzynska, K.; Trojanowicz, M. *Critical Reviews in Analytical Chemistry* **1999**, *29*, 313-321.
24. Hu, Q. F.; Yang, G. Y.; Yin, J. Y. *Talanta* **2002**, *57*, 751-756.
25. Haddad, P. R.; Doble, P.; Macka, M. *J. Chromatogr. A* **1999**, *856*, 145-162.
26. Yang, G. Y.; Zhang, C. M.; Fhu, Q.; Yin, J. Y. *Journal of Chromatographic Science* **2003**, *41*(4), 195-199.