J Fluoresc (2011) 21:321–326
DOI 10.1007/s10895-010-0719-9

ORIGINAL PAPER

Determination of Nickel(II) by CTAB Sensitized Fluorescence Quenching Method of the Derivatives of Calix[4]arene

Xiashi Zhu · Lina Ma

Received: 28 April 2010 / Accepted: 8 September 2010 / Published online: 2 October 2010

Abstract The fluorescence quenching effect of Ni^{2+} on the derivatives of p-tert- butyl-calix[4]arene with o-phenanthroline (TBCP) was studied in cetyltrimethyl- ammonium bromide (CTAB) medium. Ni^{2+} reacted with the TBCP to form inclusion complex. The fluorescence quenching was sensitized in CTAB. The linear range of calibration curve for the determination of Ni^{2+} was 0.050 μg/mL ~ 1.00 μg/mL. The detection limit estimated (S/N=3) was 5.3 ng/mL. It has been applied for the determination of Ni(II) in samples with satisfactory results.

Keywords Ni(II) · p-tert-butyl-calix[4]arene · CTAB · Sensitized · Fluorescence quenching

Introduction

Toxicological and physiological research on nickel had been a subject of growing interest over recent years. Nickel is immunotoxic and causes allergy and skin sensitization. The concentration of nickel in biological materials in populations is known to be altered by acute myocardial infarction [1]. As nickel occurs at very low levels in real samples materials, a sensitive, selective and accurate method for its determination is desirable. Useful methods include atomic absorption spectrometry(AAS) [2], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3], .high performance liquid chromatography(HPLC) [4], flow injection analysis (FIA) [5], spectrofluorimetry [6, 7], spectrophotometry [8]. Spectrofluorimetry was applied because of its high sensitivity and simplicity. And the determination of Ni^{2+} based on the fluorescence quenching of phenanthroline [9] has been reported, but the fluorescence quenching method of the derivatives of calix[4]arene for the analysis Ni^{2+} has not been established.

Calixarenes, which appeared after crown ethers and cyclodextrins as the third generation of inclusion compounds, have received much attention in extraction, ion- selective electrode, capillary electrophoresis, chromatographic and spectrographic analysis [10]. Compared with crown ethers and cyclodextrins, calixarenes have some major features [11]. There are hydrophobic cavities at the top of cup-like structure of calixarenes, which can develop inclusion complexes with neutral molecules. Similarly, there are many regular phenolic hydroxyl groups at the bottom of cup-like structure of calixarenes, which can coordinate and deliver cations [12]. Some special modified functional groups at the top or bottom of calixarene, such as p-tert-butyl [12], amido, 8-azoquinoline [13] and o-phenanthroline, are highly selective host molecules. For example, 1,10-phenanthroline is rigid and the two nitrogen atoms occupy adjacent position, which acted as a π-electron acceptor and has good coordination capacity with transition metal ions. Consequently, the change of calix[4]arene with o-phenanthroline spectrum due to coordinated with transition metal ions could be used for the determination of metal ions.

In our previous publications, the sensitizing effect of surfactant on the determination of metal ions by UV-Vis

X. Zhu (✉) · L. Ma
Department of Chemistry, Yangzhou University,
Yangzhou 225002, People's Republic of China
e-mail: xszhu@yzu.edu.cn

X. Zhu
e-mail: zhuxiashi@sina.com

spectrophotometry and spectrofluorimetry were developed [14–16]. But cetyltrimethyl-ammonium bromide (CTAB) sensitized fluorescence quenching method of the derivatives of calix[4]arene for the analysis Ni^{2+} seems to be lacking.

In this paper, the derivatives of p-tert-butyl-calix[4]arene with o-phenanthroline (TBCP, Fig. 1), which had been prepared by linking 1,10-phenanthroline to the bottom of p-tert-butyl-calix[4]arene, had the fluorescence intensity. Ni (II) could bring on the fluorescence quenching of TBCP, and there was a linear relationship between the fluorescence quenching value (ΔF) and the concentration of Ni(II). And the fluorescence intensity of TBCP (F_{TBCP}) and the fluorescence quenching value ($\Delta F=F_{TBCP}- F_{Ni\text{-}TBCP}$) were enhanced in CTAB micelle. Therefore, a novel CTAB sensitized fluorescence quenching method for the analysis Ni^{2+} has been developed.

Experimental

Apparatus and Chemicals

F-4500 fluorescence spectrophotometer (Hitachi, Japan); UV2550 spectrophotometer (Hitachi, Japan); pHS-25 type pH meter (Shanghai Precision kore magnetic Factoey)

The derivatives of p-tert- butyl-calix[4]arene with o-Phenanthroline(TBCP) was prepared by organic chemistry lab in the chemistry college of yangzhou University. A stock solution of TBCP (6.0×10^{-4} mol/L) was prepared in N,N-dimethylformamide (DMF).

A working standard solution of Ni^{2+} (10.0 μg/mL), 1.0% cetyltrimethyl-ammonium bromide (CTAB), 10% Triton X-100, 5% sodium dodecyl sulfate(SDS), 1.0×10^{-2}mol/L β-cyclodextrin (β-CD) and CH_3COOH-CH_3COONa buffer solution (pH=5.0) were employed.

All chemicals were of analytical grade.

Procedure

Measuring of Fluorescence Intensity

In a 10.0 mL volumetric flask, a quantitative working standard stock solution of Ni^{2+}, 2.0 mL CH_3COOH-CH_3COONa buffer solution (pH=5.0), 1.0 mL TBCP (6.0×10^{-4} mol/L) and 1.5 mL 1% CTAB were added. The mixed solution was diluted to final volume with distilled water, shaken thoroughly. The obtained solution was thermostated at 10.0±1°C for 10 min and the fluorescence intensity of the solution ($F_{Ni\text{-}TBCP\text{-}CTAB}$) was measured at excitation wavelength 275 nm, emission wavelength from 250–600 nm in a 1.0cm quartz cell by a F-4500 fluorospectrophotometer, and the fluorescence intensity of the blank solution ($F_{TBCP\text{-}CTAB}$) was measured at the same time. Then the fluorescence quenching value ΔF ($\Delta F=F_{TBCP\text{-}CTAB}-F_{Ni\text{-}TBCP\text{-}CTAB}$) was obtained. The excitation and emission bandwidths were set to 5 nm and 10 nm, respectively. The scan rate is 240 nm/min.

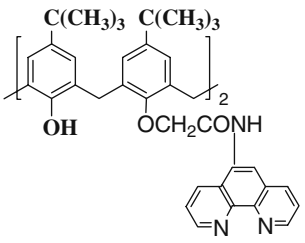

Fig. 1 The molecular formula of TBCP

The Benesi-Hildebrand Method

In this experiment, the Benesi-Hildebrand method [17] (double reciprocal plot) was used for calculating the inclusion constant (K) of Ni(II)- TBCP assuming a 1:1 inclusion model. And the expression was given by Eq. 1, where $[TBCP]_0$ was the total concentration of TBCP, ΔF was the fluorescence quenching value and α was constant. Thus, the inclusion constant (K) of the 1:1 complex, which had been calculated by dividing the intercept by the slope of the double reciprocal plot.

$$1/\Delta F = 1/(K\cdot\alpha\cdot[\mathrm{TBC}P]_0)\cdot 1/[Ni] + 1/(\alpha\cdot[\mathrm{TBC}P]_0) \quad (1)$$

Determination of Relative Fluorescence Quantum Yield

Fluorescence quantum yields of TBCP and TBCP-CTAB were measured using 0.1mg/mL L-tryptophan as reference material. Under the same apparatus conditions, according to Eq. 2 [18], the quantum yields of the analyte was calculated. Briefly, Y_s and Y_u are corresponding the standard and measurement-needed fluorescence quantum yield and F_s and F_u the integral areas of two calibration fluorescence emission curves, A_s and A_u the absorbance ($\lambda_{absorbance}=\lambda_{emission}$) of the standard and measurement-needed materials[19] and Y_s=0.14 (25°C)[20] is known.

$$Yu = Ys\times\frac{F_u}{F_s}\times\frac{A_s}{A_u} \quad (2)$$

Results and Discussion

Fluorescence Spectra

The fluorescence emission spectra of TBCP in CTAB and H_2O media are shown in Fig. 2. It could be seen that (1) the

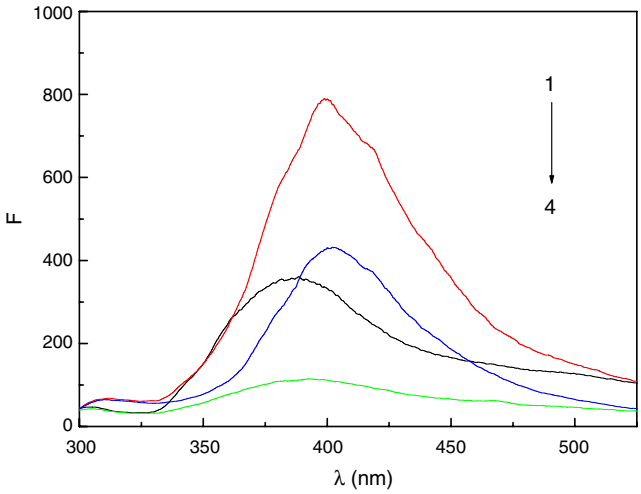

Fig. 2 Flourescence spectra. (1) TBCP (6.0×10^{-5} mol/L) + CTAB; (2) Ni^{2+} (0.35 μg/mL) + TBCP (6.0×10^{-5} mol/L) + CTAB; (3) TBCP (6.0×10^{-5} mol/L) + H_2O; (4) Ni^{2+} (0.35 μg/mL) + TBCP; (6.0×10^{-5} mol/L) + H_2O

fluorescence intensity of TBCP(F_{TBCP}) was enhanced in presence of CTAB and the maximum emission wavelength was red shifted (curve 1, curve 3); (2) the F_{TBCP} was diminished when Ni(II) was added (curve 2, curve 4) and the $F_{TBCP\text{-}CTAB}$ gradually decreased with an increase of Ni (II) concentration (Fig. 3). At the same time, the $\Delta F = F_{TBCP\text{-}CTAB} - F_{Ni\text{-}TBCP\text{-}CTAB}$ was larger than that $\Delta F = F_{TBCP} - F_{Ni\text{-}TBCP}$ with the same concentration of Ni(II). Hence, there was the sensitizing effect on the determination of Ni (II) in CTAB.

And the effect of different medium on the fluorescence quenching value (ΔF) of Ni(II)-TBCP was investigated. As could be seen in Table 1 that the order of ΔF was 1%

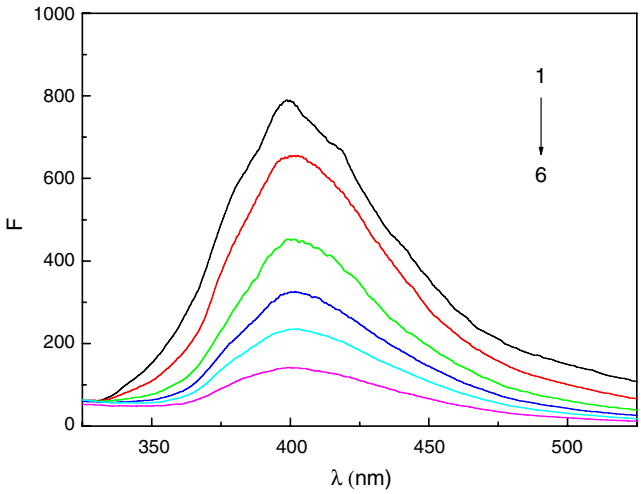

Fig. 3 Fluorescence spectra of TBCP with different concentration of Ni(II) in CTAB. (1-6) : Ni^{2+}+TBCP(6.0×10^{-5} mol/L)+CTAB, CNi : (1) 0.00 μg/mL, (2) 0.20 μg/mL, (3) 0.35 μg/mL, (4) 0.50 μg/mL, (5) 0.60 μg/mL, (6) 0.80 μg/mL

Table 1 Effect of different medium on the fluorescence quenching value

medium	ΔF
H_2O	298.01
10% Triton X-100	15.13
5% SDS	100.29
1.0×10^{-2}mol/L β-CD	196.21
1% CTAB	358.00

CTAB > H_2O > 1.0×10^{-2}mol/L β-CD > 5% SDS > 10% Triton X-100. So 1% CTAB medium was choose for this paper.

Optimization of Conditions

Effect of pH

The influence of pH on the fluorescence quenching value (ΔF) was investigated. As could be seen in Fig. 4(-⋆-), ΔF gradually enhanced with the increase of pH and ΔF reached the maximum when the pH=5.0, but it was diminished when pH>5.0.

In order to explain the influence of pH on ΔF, the change of absorbance of Ni(II)-TBCP-CTAB ($A_{Ni\text{-}TBCP\text{-}CTAB}$) with pH was investigated (Fig. 4-•-). When pH=5.0, the $A_{Ni\text{-}TBCP\text{-}CTAB}$ reached the maximum, which had the same trend with ΔF, it indicated that the formation of inclusion complex of TBCP-Ni (II) was subject to the pH, and the inclusion complex of TBCP-Ni(II) has brought about the fluorescence quenching value ($\Delta F = F_{TBCP} - F_{Ni(II)\text{-}TBCP}$). In other words, the fluorescence intensity of Ni(II)-TBCP ($F_{Ni\text{-}TBCP}$) varied with the pH, it was the reason why a sudden increasing and decreasing trend of ΔF at pH=5.0 in Fig. 4. Thus, CH_3COOH-CH_3COONa buffer solution of pH=5.0 was chosen for the determination, and 2.0 mL of the buffer solution was selected as suitable for the optimized method.

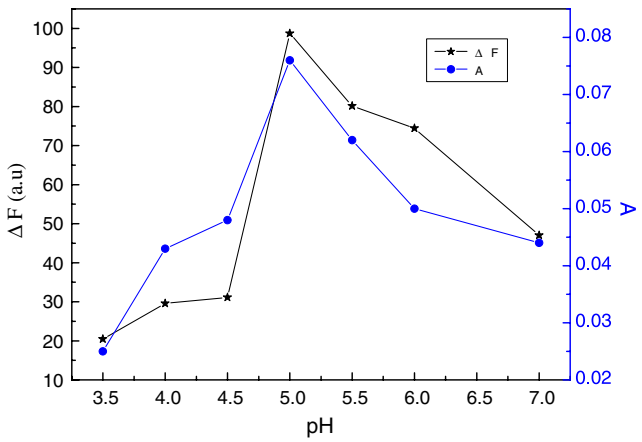

Fig. 4 Effect of pH on ΔF. C_{Ni} : 0.35 μg/mL; C_{TBCP} : 6×10^{-5} mol/L

Effect of TBCP Amount

The effect of the concentration of TBCP was tested. The results were shown in Fig. 5. ΔF reached the maximum when the amount of TBCP (6.0×10^{-4} mol/L) was 0.4 mL. Then, ΔF gradually decreased with the increase of TBCP amount due to the self-quenching of TBCP at higher concentration ($\Delta F=F_{TBCP}-F_{Ni(II)-TBCP}$). Thus, 0.4 mL TBCP ($6.0\times10^{-4}$ mol/L) was chosen for the assay.

Effect of CTAB Amount

The effect of the amount of CTAB was investigated. As was shown in Fig. 6, the ΔF reached a maximum when the amount of 1% CTAB was 1.5 mL. In this work, 1.5 mL 1% CTAB was chosen for the following experiments.

Effect of Temperature and Time

The effect of temperature on ΔF was tested (5–45°C). It was found that ΔF was steady ranging from 5 to 15°C while it was decrease with the increasing temperature. Therefore, the suitable temperature of 10±1°C was recommended for the work. At the temperature of 10±1°C, ΔF reached a maximum with the final time ranging from 5 to 30 min. So it was suitable to choose 10 min.

Effect of Foreign Substances

The effects of different foreign substrates were discussed in the determination of the 0.35 μg/mL of Ni(II). The level of tolerated concentrations of foreign substrates was considered as maximum concentration found to cause a change in signal, less than ±5%, compared with the signal for NI(II) alone. The tolerance limits are shown in Table 2. It was observed that most of the common metal ion did not influence the determination of Ni(II).

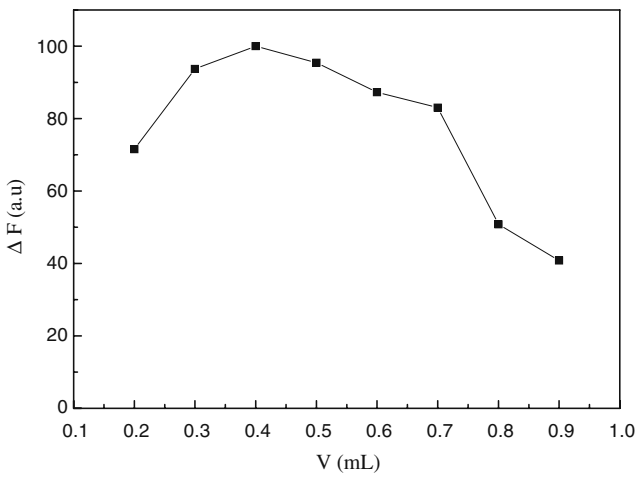

Fig. 5 Effect of the amount of TBCP on ΔF. C_{Ni} : 0.35 μg/mL

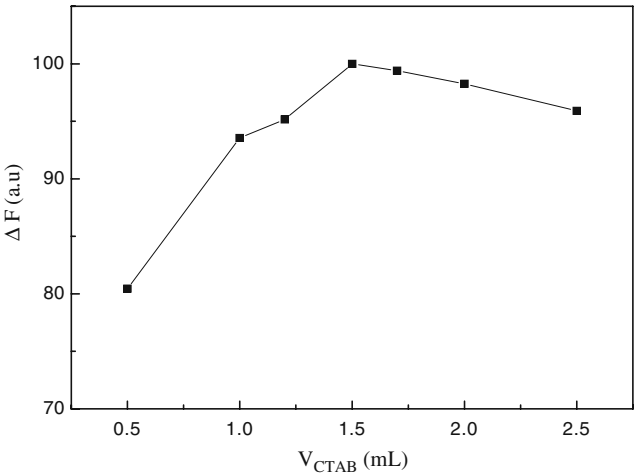

Fig. 6 Effect of the amount of CTAB on ΔF. C_{Ni} : 0.35 μg/mL; C_{TBCP} : 2.4×10^{-5} mol/L

Analytical Performance

Under the optimum conditions, the linear regression equation was determined to be: ΔF=159.62+626.32C (μg/mL), R=0.992. A linear relationship was observed over the range of 0.05~1.00 μg/mL. The detection limit estimated (S/N=3) was 5.3 ng/mL.

Sample Analysis

The proposed method was satisfactorily applied to the determination of amount of Ni^{2+} in standard sample (GBW 08618) and tap water. Analyses were carried out following the general procedure. In the determination analysis of standard sample (n=3), the measured value (0.212± 0.030 μg/mL) is in good agreement with the certified values (0.206±0.001 μg/mL).

Table 2 Effect of interfering substances on the determination of Ni (II) (Ni(II): 0.35 μg/mL)

Tested substrates	Tolerance limit (μg/mL)	Tested substrates	Tolerance limit (μg/mL)
Pb^{2+}	1.0	Co^{2+}	0.30
Cd^{2+}	0.35	Al^{3+}	1.0
Zn^{2+}	1.0	Fe^{3+}	2.0
Cu^{2+}	0.35	K^{+}	200.0
Mg^{2+}	1.0	NO_3^{-}	200.0
Mo(VI)	1.0	Cl^{-1}	200.0
Cr(VI)	0.60	SO_4^{2-}	1.6

The standard addition method was also used to the determination of trace amount of Ni(II) in tap water sample. The recovery ratio was ranging from 96.3% to 99.5% which was satisfactoried to experiments in Table 3.

Discussion of Sensitizied Mechanism

The Interaction of TBCP and Ni(II)

TBCP is an easy-to-selective modification of both the upper and lower edge, with the benzene ring units composed of hydrophobic cavities, which has a truncated cone structure which could tie with ionic object or pack neutral molecules. This special molecular structure could include metal ions (Ni^{2+}) which had matched polarity, size, shape and property into their hydrophobic cavities to form inclusion complexes, which may affect the fluorescence intensity of TBCP.

According to the Benesi-Hildebrand method, it was found that the double reciprocal plot had good linear relationships (R=0.9982, Fig. 7), which could support the formation of a 1:1 complex. And the inclusion constant K was 151605 L/mol. The larger the value of K suggested that the more stable inclusion complex. As a result of the inclusion effect of TBCP and Ni(II) brought about dynamic fluorescence quenching. Namely, Ni^{2+} was the quencher which could bring out the decrease of the fluorescence intensity of TBCP.

The Sensitizing Effect of the CTAB Surfactant

Generally speaking, it was demonstrated that the sensitizing effect of CTAB on spectrofluorimetry rested on two factors: (1) the solubilization capacity and (2) the microenviroment of medium [21, 22]. In order to discuss the influence of the microenvironment on the fluorescence intensity of TBCP, the fluorescence quantum yields of Y_u in various media were determined, respectively. The fluorescence quantum yield was one of the mostly basic and significant parameters in all the characters of fluorescence substance

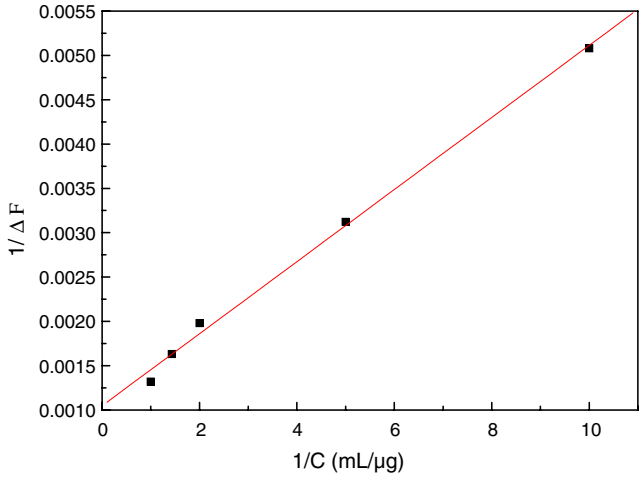

Fig. 7 Double reciprocal plot of Ni(II) in TBCP. C_{TBCP} : 2.4×10^{-5} mol/L

[14]. It represented the ability of translating absorption energy to fluorescence. In this paper, the fluorescence quantum yield of TBCP(Y_u) in water and CTAB were determined, the results were 0.00559 and 0.0187, respectively. The quantum yield Y_u was approximately 2.34 times higher in the presence of CTAB than in the absence of CTAB. The Y_u value was tightly related to chemical structure and microenvironment of the system [19]. The Y_u value is higher, the ability of translating absorption energy to fluorescence is stronger, it was also a reason of enhanced determination sensitivity in CTAB. The fluorescence intensity of TBCP must enhance with the increase of fluorescence quantum yield of TBCP in CTAB micelle. So, ΔF was increase with the increment of fluorescence intensity of TBCP ($F_{TBCP}\uparrow$, $\Delta F\uparrow$). The fluorescence intensity of TBCP was higher in the CTAB micelle than that in H_2O medium because of the CTAB micelle could better accommodate the microenvironment. In other words, CTAB micelle was able to decrease the self fluorescence quenching of TBCP and the fluorescence quenching effort of the external quencher. So, CTAB had sensitizing effect on the fluorescence quenching value (ΔF) of the Ni(II)-TBCP system.

Table 3 Determination results of tap water

Sample	Added(μg/mL)	Found (μg/mL)	Recovery(%)
Tap water	0	ND	0
	0.10	0.0963	96.3%
	0.20	0.195	97.6%
	0.30	0.298	99.5%
	0.40	0.392	98.0%

ND

Conclusion

In this paper, the fluorescence intensity of TBCP was quenched due to Ni(II) reacted with TBCP to form a complex, and the fluorescence quenching value (ΔF) was increase in CTAB. Based on this, a novel fluorescence quenching method for the determination of Ni(II) has been developed. The method has been applied for the determination of Ni(II) in samples with satisfactory results.

References

1. Yang XR, Qiao ZC, Wei WZ, Yao SZ (1998) Determination of nickel in human urine by ion chromatography with series bulk acoustic wave detection. Talanta 46:697–702
2. Ding DM (2006) Comparative study of GFAAS and ICP-AES in the Determination of Nickel in Water. Chin J Spectrosc Lab 23 (6):1244–1246
3. Xu YY, Zhou JF, Wang GX, Zhou JF, Tao GH (2007) Determination of trace amounts of lead, arsenic, nickel andcobalt in high-purity iron oxide pigment by inductively coupled plasma atomic emission spectrometry after iron matrix removal with extractant-contained resin. Anal Chim Acta 584:204–209
4. Ding ZW, Li HB (1998) Separation and determination of iron(II), cobalt(II) and nickel(II) by Re-HPLC. Chin J Anal Chim 26 (10):1284–1284
5. Qu XJ, Zhou J, Yin HZ (1997) Simultaneous determination of nickel and iron by flow injection-spectrophotometry. Chin J Anal Chim 25(2):168–171
6. Eric RD, Lester AS (1987) Determination of sulfur, nickel and vanadium in fuel and residual oils by x-ray fluorescence spectrometry. Anal Chim Acta 192:361–366
7. Bourson J, Badaoui F, Valeur B (1994) Coumarinic fluorescent chemosensors for the detection of transition metal ions. J Fluoresc 4(4):275–277
8. Mohammad AT, Ali MD, Bal KP, Swati P (1998) Derivative UV-visible spectrophotometric determination of nickel in alloys and biological samples after preconcentration with the ion pair of 2-nitroso-1-naphthol-4-sulfonic acid and tetradecyldimethylbenzylammonium chloride onto microcrystalline naphthalene or by a column method. Anal Chim Acta 367:55–61
9. Xiang HY, Chen XM, Li SQ, Zhang J (2000) Determination of nickel based on the fluorescence quenching of phenanthroline. Chin J Spectrosc Spectra Anal 20(4):566–568
10. Lin L, Wu CY (1997) Applications of calixarene derivatives in analytical chemistry. Chin J Anal Chim 25(5):850–856
11. Hu XB, Zhong ZL, Lu XR, Chen Y-Y (1997) The researching progress of calixarenes and crown ether. Chin. J. Chem. Bull (4): 18–25
12. Gao B, Feng YQ, Zhou LX, Ma X (2004) Progress of inclusion property of calixarene. Chin J Org Chem 24 (7):713–721
13. Ma QL, Ma HM, Su MH, Wang ZH, Nie LH, Liang SC (2001) Determination of nickel by a new chromogenic azocalix[4]arene. Anal Chim Acta 439:73–79
14. Zhu XS, Bao L, Guo R, Wu J (2004) Determination of aluminium (III) in water samples in a microemulsion system by spectrofluorimetry. Anal Chim Acta 523:43–48
15. Bao L, Zhu X.S, Guo R (2006) Simultaneous determination of cobalt and nickel by microemulsion sensitization-dual wavelength spectrophotometry. Chin. J. Anal Instrum (2):34–38
16. Wu J, Gu Y, Zhu X.S (2008) Determination of trace lanthanum (III) by β-cyclodextrin sensitized UV-Vis spectrophotometry. Chin. J. Anal. Instrum (3): 47–51
17. Vimal KB, Ajay PSP, Narinder S, Maninder SH, Geeta H (2002) Synthesis of new tripodal receptors-a 'PET' based 'off-on' recognition of Ag^{+}. Tetrahedron 64(20):5384–5387
18. Zhao J, Wei YJ (2006) Fluorescence spectra and fluorescence quantum yield of triton X-100. Chin J Spectrosc Spectra Anal 26 (8):1523–1525
19. Zhu XS, Gong AQ, Yu SH (2008) Fluorescence probe enhanced spectrofluorimetric method for the determination of gatifloxacin in pharmaceutical formulations and biological fluids. Spectrochim Acta Part A 69:478–482
20. Zhang YP, Wei YJ, Li N, Qin SJ (2004) Fluorescence quantum yield of human and bovine serum albumin. Chin J Anal Chim 32 (6):779–782
21. Zhu XS, Guo R, Qi W-B (1995) Study on the mechanism of sensitized reaction of oil/water microemulsion. Chin J Anal Chem 23(9):989–992
22. Zhu XS, Guo R, Kang C, Shen M (1995) Sensitized Reaction of built-up O/W microemulsion on Fe(III)-BPHA and mechanism. Chin J Acta Chim Sinica 53:716–720