

Synthetic and Analytical Application of 5-(4-Sodium Sulphonatephenylazo)-8-(p-Toluenesulphonamido) Quinoline

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Abstract: A new spectrofluorimetric reagent, 5-(4-sodium sulphonatephenylazo)-8-(p-toluenesulphonamido) quinoline (SPTSQ) has been synthesized, and its identity has been confirmed by infrared spectrometry, thermogravimetry and elemental analysis. Its chromogenic and fluorimetric properties and reactivities with metal ions have been investigated. A simple, rapid, selective and sensitive new spectrophotometric method for determination of copper is developed. In the presence of cetyltrimethyl ammonium bromide cationic surfactant (CTMAB), SPTSQ reacts with copper to form a violet-red 1:2 (metal:ligand) complex with an absorption maximum at 585 nm. Beer's law is obeyed over the concentration range 0~0.8 $\mu\text{g/mL}$ copper. The molar absorptivity and sandell's sensitivity of the method are $8.5 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $0.00075 \mu\text{g} \cdot \text{cm}^{-2}$, respectively. The interference of various ions has been studied and the method has been used for the determination of microamount of copper in crude lead and alloys.

Key words: synthesis; 5-(4-sodium sulphonate phenylazo)-8-(p-toluenesulphonamido)-quinoline; copper; spectrophotometry

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5-(4-磺酸钠苯基偶氮)-8-(对-甲苯磺酰氨基)喹啉的合成及其分析应用

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摘要: 合成了一种光度荧光新试剂, 5-(4-磺酸钠苯基偶氮)-8-(对-甲苯磺酰氨基)喹啉(SPTSQ), 其结构经红外光谱、热重分析和元素分析确证。研究了试剂及其与金属离子的显色反应和荧光反应特性。建立了一种简单、灵敏、快速、选择性的光度测定铜的新方法。在阳离子表面活性剂溴化十六烷基三甲铵存在下, SPTSQ与Cu(II)形成2:1的紫红色络合物, 其最大吸收峰位于585 nm, 铜在0~0.8 $\mu\text{g} \cdot \text{mL}^{-1}$ 浓度范围内符合比尔定律。摩尔吸光系数和桑德尔灵敏度分别为 $8.5 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ 和 $0.00075 \mu\text{g} \cdot \text{cm}^{-2}$ 。研究了不同离子的干扰, 该法已用于粗铅和合金样品中微量铜的测定。

关键词: 合成; 5-(4-磺酸钠苯基偶氮)-8-(对-甲苯磺酰氨基)喹啉; 铜; 分光光度法

1 INTRODUCTION

It has long been the goal of both organic and analytical chemists to find new spectrophotometric and fluorimetric reagents which are selective and sensitive for particular metal ions. A large number of functional groups have been found to very useful, such as (O,O), (S,S), and (N,N) ligands. The derivatives of 8-hydroxy-

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(8HQ) or 8-mercaptoquinoline(8MQ), they have been widely used for spectrophotometric and fluorimetric determination of various metal cations^[1]. However, 8-amino derivatives of quinoline (8AQ) has received very little attention, only a few published papers^[2,3]. Because 8-aminoquinoline has (N,N) as its chelating atom, it is more selective than 8HQ(N,O) and 8MQ(N,S). A search of the literature failed to reveal the use of the 8-sulfonamidoquinoline azoderivatives in analytical chemistry, since they possess not only abovementioned (N,N) chelating atom, but the acid strength of the sulfonamido group ($-\text{SO}_2-\text{NH}-$) is about the same as a phenolic hydroxyl group, it is hoped that these derivatives might prove as useful as 8HQ or 8MQ, in metal analysis. With this in mind a series of 8-amino- and 8-sulfonamidoquinoline azoderivatives have been prepared^[4], including 5-(4-nitrophenylazo)-8-aminoquinoline (p-NPAQ), 4-(arsenophenylazo)-8-aminoquinoline(APAQ), sodium 7-phenyl azo-8-aminoquinoline-5-sulphonate(SPAAQ), 5-(4-methoxyphenylazo)-8-(p-toluenesulfonamido)quinoline(NPTSQ) and 5-(4-methoxyphenylazo)-8-(p-toluenesulfonamido)quinoline (MOPTSQ). Some of them have been used in the fluorimetric analysis of copper, cobalt and gold, and spectrophotometric determination of cobalt, platinum, palladium and gold^[5-8]. A thorough survey of the literature showed that no previous attempt has been made to employ 8-sulfonamidoquinoline azoderivatives for the spectrophotometric determination of copper. In this paper, the synthesis of 5-(4-sodium sulphonatophenylazo)-8-(p-toluenesulfonamido)quinoline (SPTSQ) is reported at first and proposed as a new reagent for the spectrophotometric determination of copper in aqueous solution. Various parameters such as pH, reagent concentrations and interference of foreign ions have been studied. This method has been applied to the determination of copper in crude lead and alloys. The reagent has been found to be sensitive and selective compared with other chromogenic agents.

2 EXPERIMENTAL

2.1 Apparatus

The Shimadzu(Japan) UV-265 spectrophotometer and a Model 721 spectrophotometer(Third Analytical Instrument Factory, Shanghai) were used for recording spectra and absorbance measurements in a quartz cell of 1-cm path length. A Model S-2 pH meter was used for pH measurements and a Shimadzu(Japan) RF-540 fluorimeter for fluorescence measurements.

2.2 Reagents

Synthesis of 5-(4-sodium sulphatophenylazo)-8-aminoquinoline (SPAQ). Sulphanilic acid (1.1g) was dissolved in 2mL of ice-cold concentrated hydrochloric acid, 5ml of ice-cold distilled water and slowly diazotized with a solution of 0.4g of sodium nitrite in 5ml of water. The diazotized solution was then added dropwise with stirring to an ice-cold solution of 8AQ(0.8g) in 30 ml of $2\text{mol}\cdot\text{L}^{-1}$ acetic acid, $2\text{mol}\cdot\text{L}^{-1}$ sodium hydroxide being added to keep the pH constant, and the mixture was left for 1hr., with stirring in the ice-bath, the neutralized with sodium hydroxide and filtered. The red precipitate was recrystallized and salted out with sodium chloride several time from water to give needle shaped crystals. Dried at about 100°C for 5hr., and with a yield of 72%. Elemental analysis was as follows: calculated ($\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_4\text{SNa}$), C51.43, H3.14, N 16.00, S9.14% found, C51.51, H3.11, N15.89, S9.22%.

Synthesis of SPTSQ. SPAQ(1.0g) was placed in a 25 mL three-necked flask and dissolved in 10mL of pyridine. The flask was fitted with a motor stirrer and immersed in an ice water bath, 0.7g of p-toluenesulfonyl chloride was added in small portions over 2.5hr. with the solution being stirred throughout. The reaction mixture was then poured into 30 ml of cold water with vigorous stirring. Then neutralized with concentrated hydrochloric acid and filtered. The precipitate was salted out with sodium chloride several times from water and a violet crystalline substance was obtained. Yield of 70%. Elemental analysis was as follows: required ($\text{C}_{22}\text{H}_{17}\text{O}_5\text{N}_4\text{S}_2\text{Na}\cdot\text{H}_2\text{O}$), C50.57, H3.64, N10.73, S12.26%; found, C50.46, H3.69, N10.99, S12.11%. The data obtained

from thermogravimetry, infrared and nuclear magnetic resonance spectra confirmed the structure of SPTSQ to be as shown in Fig. 1. The acid dissociation constants of SPTSQ were calculated by spectrophotometric method,

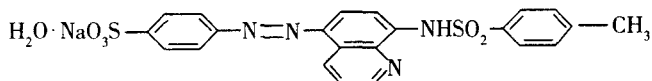


Fig. 1 Structure of SPTSQ confirmed by data obtained from TG, IR and NMR spectra

only two of the three structurally possible pK values were determined, namely $\text{pK}_{\text{a}2} = 3.6$ and $\text{pK}_{\text{a}3} = 7.8$. The first dissociation step takes place in very strongly acidic medium and could not be determined with the glass electrode used for monitoring the pH.

SPTSQ solution, $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. A 0.0528 g amount of SPTSQ was dissolved in 500 mL of distilled water. The solution is stable for ten months at least. Stock copper solution, 100 ppm. Prepared by dissolving 0.1 g of pure copper metal in nitric acid (1 + 2) and diluting to 1 L with distilled water. Working solution were prepared by accurate dilution of the stock solution.

Cetyltrimethyl ammonium bromide (CTMAB) solution, $0.01 \text{ mol} \cdot \text{L}^{-1}$. Prepared by dissolving the substance in water.

Buffer solution, pH 10.5. Prepared from 0.1 borax solution, the pH being adjusted with $0.1 \text{ mol} \cdot \text{L}^{-1}$ sodium hydroxide solution.

All other reagents were of analytical - reagent grade unless stated otherwise.

2.3 Procedures

Spectrophotometric determination of copper. Pipette a known volume of solution containing up to $20 \mu\text{g}$ of copper in a 25 mL calibrated flask, add 3 mL of SPTSQ solution, 2.5 mL of CTMAB solution and 3.0 mL borax solution, dilute to the mark with distilled water, mix. And let stand for about 5 min. Measure the absorbance at 585 nm against a reagent blank prepared in the same manner.

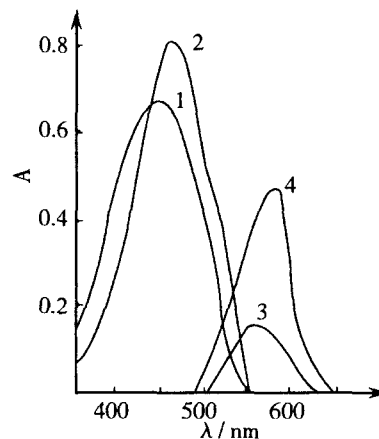
Determination of copper in crude lead. Take 0.5 ~ 1.6 g of crude lead into a beaker, add 20 mL of nitric acid (1 + 3) to dissolve by slightly heating, evaporate the solution to incipient dryness, the residue is dissolved in water, the add 5 mL of sulphatic acid (1 + 1) to precipitate lead. Filter off the residue and wash it with distilled water, collecting the filtrate and washings in a 100 mL standard flask, dilute to the mark with distilled water. Pipette 1.0 mL of the solution in a 25 mL calibrated flask and subsequently pipette 2 mL of 10% tartaric acid solution. Adjust the pH with $1.0 \text{ mol} \cdot \text{L}^{-1}$ sodium hydroxide solution to about 10.5 and complete the determination as above.

Determination of copper in zinc and aluminium alloys. Weigh accurately 1.0 g the zinc or aluminium alloy samples and dissolve in 20 mL of nitric acid (1 + 1), evaporate the resulting solution to incipient dryness, add 2 mL of hydrochloric acid (1 + 1), then dilute with distilled water to 1.0 L. Take a suitable aliquot in a 25 mL calibrated flask, add 0.5 mL 2% sodium fluoride solution and complete the determination as above.

3 RESULT AND DISCUSSION

3.1 Absorption spectra

In the presence of CTMAB, copper reacts with SPTSQ to form a violet - red complex whose absorption spectrum is shown in Fig. 2. The reagent blank exhibits a maximum absorption at 465 nm, and the Cu(II) - SPTSQ - CTMAB system shows a maximum absorption at 585 nm, where the reagent blank gives almost zero absorption. Hence, in all instances the absorption was measured at 585 nm against a corresponding reagent blank.



- (1) SPTSQ (against water as reference)
- (2) SPTSQ - CTMAB (against water)
- (3) SPTSQ - Cu(II) complex (against 1)
- (4) SPTSQ - Cu(II) - CTMAB (against 2)

Fig. 2 Absorption spectra

3.2 Reaction conditions

The effect of pH on the colour system was tested. The optimum pH range was 9.0 – 12.0, and a borax buffer solution (pH10.5) was selected for the colour reaction. Addition of 2.0 – 4.0mL buffer solution to an approximately neutral test solution was found to give essentially the constant absorbance, and addition of 3.0mL is recommended.

In the absence of surfactant or the presence of nonionic or anionic surfactants, the colour system gives a low absorbance, but the presence of a cationic surfactants, the absorbance increases markedly (Table 1). CTMAB is the best additive, 1.5 – 4.0mL of 0.01mol·L⁻¹ CTMAB solution gives good results; a volume of 2.5mL is recommended.

Maximum and stable absorbance was attained with 2.0 ~ 4.0 mL of SPTSQ and use of 3.0mL is selected as optimal.

At room temperature, the maximum absorbance is obtained 5min. after the mixing of the components, and it is stable for 12hr. at least. The order of addition of reagents seriously affects the system, however. Addition in Cu(II), borax buffer solution, CTMAB solution and SPTSQ solution produces metal hydroxide precipitation, whereas the order Cu(II), SPTSQ, CTMAB and borax buffer solution gives the best result.

3.3 Analytical characteristics

A calibration graph was prepared by the procedure described for determination of microamounts of copper, Beer's law was obeyed over the concentration range 0 ~ 20ug of copper in 25mL of final solution; the linear regression equation obtained was

$$A = 0.053 1C + 0.001 2 \quad (r = 0.999 9)$$

Where C is expressed as $\mu\text{g}/25\text{mL}$. From this equation, the molar absorptivity(ϵ) and Sandell's sensitivity (s) of the method was calculated to be $8.5 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $0.000 75 \mu\text{g} \cdot \text{cm}^{-2}$, respectively. The standard deviation for ten replicate determination of 10 ug of copper was 0.012 μg .

The composition of the complex was determined by the molar – ratio and continuous – variation methods , and found to 1:2(metal:ligand).

3.4 Interference

The influence of 39 diverse ions on the determination was examined. The ions tested were added individually to a solution containing 10ug of copper. A maximum error of 2% in the absorbance reading was considered tolerable.

Table 2 Tolerance limits in the determination of 10 μg Cu(II) with SPTSQ

Ion added	Amount tolerated / μg	Ion added	Amount tolerated / μg
Cl ⁻ , NO ³⁻	10 000	Mo(VI), Cd(II)	400
F ⁻ , SO ₄ ²⁻	5 000	Fe(III) * , Sn(IV), Hf(IV)	300
acetate, tatarate	2 000	SiO ₃ ²⁻ , PO ₄ ³⁻	250
Ca(II), Al(III) *	1 500	Th(IV), V(V), Ce(IV)	200
Zn(II), Pb(II) &	1 000	Hg(II), Mn(II), Sr(II)	150
W(VI), Mg(II)	600	Pt(II), Ge(IV), Zr(IV), As(III)	100
Bi(III), Ti(IV)	500	Ag(I), Ga(IV)	50
Ba(II), Cr(VI)	450	Au(III)	20

The tolerance limit of foreign ions is given in Table 2. The interference from Fe³⁺, Al³⁺ can be eliminated by masking with sodium fluoride, and the interference of Pb²⁺ was eliminated by masking with tataric acid, Thus the data in Table 2 indicate the reasonable selectivity of this method in the presence of associated ions.

* Masked with 5mg of sodium fluoride & Masked with 2mg of tataric acid

3.5 Applications

In order to confirm the usefulness of the proposed spectrophotometric method, it has been applied to the determination of microamounts of copper in crude lead, zinc and aluminium alloys. The results are shown in Table 3. The copper contents obtained are all in good agreement with the certified values for copper.

Table 3 Determination of microamounts of copper in crude lead, zinc and aluminium alloys

Sample	Certificat value for copper/%	Copper found/%	Recovery/%
Aluminium alloys			
NB72	0.240	0.243	101
BY 2144	0.094	0.095	99
Zinc alloys			
YN 793	1.30	1.35	103
YN799	1.50	1.47	99
Crude lead			
No.1	0.250	0.249	97
No.2	0.110	0.108	98

* Values obtained by atomic - absorption spectrometry

4 CONCLUSION

The comparison (in Table 4) of the SPTSQ method with others shows the proposed method for spectrophotometric determination of copper has the advantages of higher sensitivity, reasonable selectivity, and low absorbance of the reagent blank. It does not require heating and extraction with organic solvents and it can be applied to the determination of microamounts of copper in a wide range of materials.

Table 4 Comparison of some reagents for spectrophotometric determination of copper

Reagent	λ_{\max}/nm	$\epsilon/L \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	Medium	Reference
BCHODH	600	1.6×10^4	Aqueous	9
PAR	510	8.0×10^4	HCCl ₃	10
TDMABA	590	4.6×10^4	Aqueous	11
CPR	490	2.2×10^4	Aqueous	12
HQANB	430	5.4×10^4	Aqueous	13
SPTSQ	585	8.5×10^4	Aqueous	This work

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