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Study on Colour Reaction of Chromium(III) with 2-(2-Quinolinylazo)-resorcin using Microwave Radiation and its Application

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A sensitive, selective and rapid method has been developed for the determination of chromium based on the colour reaction of Cr(III) with 2-(2-quinolinylazo)-resorcin (QAR). The Cr(III) can forms complex with QAR very slow at pH 5.5. However, irradiating the reacting mixture with microwave energy can markedly accelerate the complex formation. The absorbance reaches its maximum with 5 min of irradiation and remained stable at least for 24 h. Cetyl trimethyl-ammonium bromide (CTMAB) was used for increasing the sensitivity and solubility of the system. The molar absorptivity of the complex is 8.94×10^4 L mol^{-1} cm^{-1} at 590 nm. Beer's law is obeyed in the range of 0.01-0.8 µg/mL. This method was applied to the determination of chromium(III) in biological samples, water and steel with good results.

Key Words: 2-(2-Quinolinylazo)-resorcin, Chromium, Spectrophotometry, Microwave radiation.

INTRODUCTION

Chromium is an important element, not only for industry, but for biological systems as well[1-3]. In rapidly expanding analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop simple, sensitive and selective analytical methods that do not use expensive or complicated test equipment. Many sensitive and selective instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence, have widely been applied to the determination of chromium[4-9]. The spectrophotometric methods have gained popularity because of their simplicity and low operating costs[10-16]. However, few methods

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for chromium determination are based on the complex formation with Cr(III) in aqueous solution because the slow reactions of chromium(III) aquo-complexes[17-21] $[Cr(H_2O)_6]^{3+}$.

In previous work, some 2-quinolylazo reagents were reported for the determination of metal ions[22-25]. This type of reagent has higher sensitivity than pyridylazo or thiazole reagents because of its larger conjugated system. However, the utilization of 2-quinolylazo reagents for the determination of chromium has not been reported yet. Microwave energy has been applied to the field of chemistry, primarily dealing with rapid sample dissolution in analytical chemistry and acceleration of reactions in organic chemistry[26,27]. In addition, microwave irradiation can be used to accelerate some colour-forming reactions for spectrophotometric determinations[20,21,28]. Spectrophotometric determination of chromium using EDTA[20] or TAR[21] as the colour-forming reagent with microwave radiation has been reported. However, the method has a low sensitivity and selectivity.

In this paper, to develop a more sensitivity and selectivity method for chromium(III) determination, we studied the colour reaction of 2-(2-quinolinylazo)-resorcin (QAR) with chromium(III) using microwave radiation. Based on this, a highly sensitive, selective and rapid method for the determination of chromium in biological samples, water and steel samples was developed.

EXPERIMENTAL

A UV-160A spectrophotometer (Shimidzu, Japanese) equipped with 1 cm cells was used for all absorbance measurements. The pH values were determined with a Beckman F -200 pH meter. A microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China) was used for heating the sample solutions.

All the solutions were prepared with ultra-pure water obtained by a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA).

2-(2-Quinolinylazo)-resorcin (QAR) was synthesized by according to the previous literature[29,30] and a 4.0×10^{-4} mol/L of QAR solution was prepared by dissolving QAR with ethanol. A stock standard solution of chromium (1.0 mg/mL) was obtained from the Chinese Standard Center, and a work solution of 2.0 µg/mL was prepared by diluting this solution. Acetic acid-sodium acetate (HOAc-NaOAc) buffer solution (0.5 mol/L, pH = 5.5, containing 0.1 mol/L Na_2EDTA and 0.5 mol/L NH_4F) was prepared by dissolving 68 g of trihydrate sodium acetate, 32.7 g of ethylenediamine tetraacetic acid disodium salt ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) and 20.5 g NH_4F in 600 mL of water, then the solution was neutralized to pH 5.5 with glacial acetic acid and diluted to the volume of 1000 mL. Cetyl trimethylammonium bromide (CTMAB) solution (2.0 % (w/v)) was prepared by dissolving

CTMAB with ethanol. Hydroxylammonium chloride solution 5 % (w/v) was prepared by dissolving 5.0 g of hydroxylammonium chloride in 100 mL of water. All chemicals used were of analytical grade unless otherwise stated.

General procedure: To a standard or sample solution containing no more than 20 µg of Cr(III) in a 25 mL of calibrated flask, 1 mL of hydroxylammonium solution (5 %) was added to guarantee quantitative chromium reduction to Cr(III). Then 4.0 mL of HOAc-NaOAc buffer solution (containing 0.1 mol/L Na_2EDTA and 0.5 mol/L NH_4F), 2.0 mL of 4.0×10^{-4} mol/L QAR solution and 1.0 mL of 1.0 % CTMAB solution were added. The mixture was approximately diluted to a volume of 25 mL and placed on the center of the microwave oven. So, the solution was heated up with the microwave oven operating on full power (1000 W) for 5 min to promote the complex reaction. After cooling, the solution was diluted to the volume of 25 mL. The absorbance of this solution was measured at 590 nm in a 1 cm cell against a reagent blank prepared in a similar way without chromium.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of QAR and its Cr(III) complex under the optimum conditions are shown in Fig. 1. The absorption peaks of QAR and its complex at pH 5.5 are located at 460 nm and 590 nm, respectively.

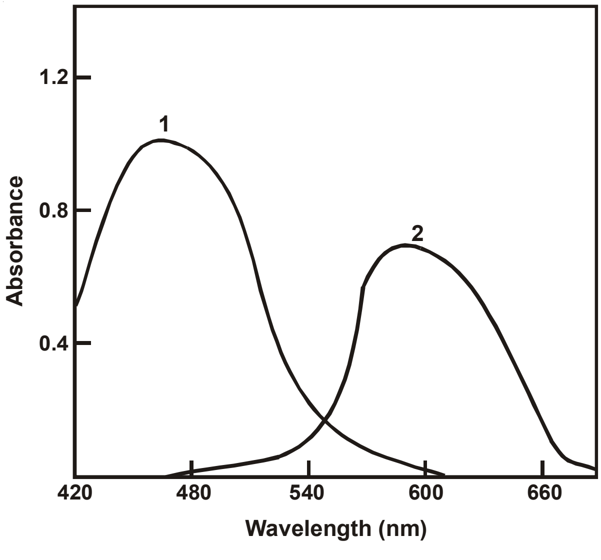

Fig. 1. Absorption spectra of 2-(2-quinolinylazo)-resorcin (QAR) and its Cr(III) complex: 1 QAR-CTMAB blank against water; 2 QAR-Cr(III)-CTMAB complex against reagent blank

Effect of acidity: The results showed that the optimal pH for the reaction of Cr(III) with QAR is 4.5-6.5. A HOAc-NaOAc buffer solution of pH 5.5 was recommended to control the pH. As the use of 3.5-5.0 mL of the buffer solution per 25 mL of final solution was found to give a maximum and constant absorbance. The use of 4.0 mL buffer solution was recommended. The buffer solution containing 0.08-0.15 mol/L of Na_2EDTA and 0.4-0.6 mol/L of NH_4F could markedly increase the selectivity of this system. (Without Na_2EDTA and NH_4F in the buffer solution, the tolerance limits of foreign ions were 0.01 mg for Cu(II), Fe(III), Zn(II); 0.005 mg for Sn(IV), Pd (II), Co(II), Ni(II). However, the tolerance limits of foreign ions reached 10 mg for Fe(III); 0.5 mg for Cu(II), Zn(II); 0.2 mg for Co(II), Ni(II), Sn(IV); 0.1 mg for Pd(II) when Na_2EDTA and NH_4F were present in the buffer solution). Therefore, 0.1 mol/L of Na_2EDTA and 0.5 mol/L of NH_4F in the buffer were recommended.

Effect of surfactants: The Cr(III)-QAR complex has a poor solubility in water solution. One needed to add a suitable amount of surfactants to enhance the solubility of the complex. Experiments showed that all the anionic surfactants, nonionic surfactants and cationic surfactants enhanced the solubility. In addition to enhancing the solubility, in the nonionic surfactants and cationic surfactants medium, the sensitivity of the Cr(III)-QAR chelates was increased markedly too. The effect of the nonionic surfactants and cationic surfactants improving the sensitivity is shown in Table-1. The results show that CTMAB was the best additive and the use of 0.6-2.0 mL of CTMAB gives a constant and maximum sensitivity. Accordingly, 1 mL CTMAB solution was recommended.

TABLE-1
EFFECT OF SURFACTANTS ON Cr(III)-QAR CHROMOGENIC SYSTEM

Surfactant	Absence	CTMAB	CPB	Triton-X-100	Tween-80	Tween-20	SDS
λ_{max} (nm)	565	590	585	580	580	580	560
ε ($\times 10^4$) (L mol^{-1} cm^{-1})	5.46	8.49	8.04	7.18	7.04	7.22	4.92

Effect of QAR concentration: For up to 20 µg of Cr(III), the use of about 2.0 mL of 4.0×10^{-4} mol/L of QAR solution has been found to be sufficient for a complete reaction. Accordingly, 2.0 mL of QAR solution was added in all further measurements.

Effect of heating with microwave irradiation: Chromium(III) does not react with QAR at room temperature due to inertness of $[Cr(H_2O)_6]^{3+}$. However, a complex is formed on heating the reactants. Under experimental conditions it was studied the effect of microwave irradiation on the coordination reaction between QAR and Cr(III). The solution was heated with the microwave oven operating on full power (1000 W) at different times (1 to 8 min). As constant absorbance was recorded on irradiation for 4-8 min, all determinations were carried after irradiation for 5 min. The complex was stable for at least 24 h.

Calibration curve and sensitivity: The calibration curve shown that Beer's law is obeyed in the concentration range of 0.01-0.8 µg Cr(III) per mL. The linear regression equation obtained was: A = 1.72 C (µg/mL) + 0.0189, (r = 0.9995). The molar absorptivity was calculated to be 8.94×10^4 L mol^{-1} cm^{-1} at 590 nm.

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 Cr(III) to 2-(2-quinolinylazo)-resorcin (QAR) is 1:2.

Interference: The selectivity of the proposed method was investigated by the determination of 5.0 µg/25 mL of Cr(III) in the presence of various ions within a relative error of ± 5 %. The results are given in Table-2. Results show that Ag(I) and Pt(IV) give serious interferences. These interferences can be eliminated by masking with NH_4SCN. This method is highly selective.

TABLE-2
TOLERANCE LIMITS FOR THE DETERMINATION OF 5 µg OF Cr(III) WITH QAR (RELATIVE ERROR ± 5 %)

Ion added	Tolerate (mg)
NO_3^-, K^+, BO_3^{3-}, Tartaric acid	80.000
Li^+, Al^{3+}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, ClO_4^-	30.000
Ca^{2+}, Mg^{2+}, BrO_3^-, ClO_3^-, Fe^{3+}	10.000
SO_3^{2-}, Sr^{2+}, Ba^{2+}, IO_3^-, B(III)	5.000
Mn^{2+}, Ce^{4+}, W^{6+}, Mo^{6+}	2.000
Ti^{4+}, Bi^{3+}, Zr^{4+}, Zn^{2+}, Cu^{2+}	0.500
Tl^{3+}, Cd^{2+}, Sn^{4+}, Co^{2+}, Ni^{2+}, Pt^{4+}*, Ag^+*	0.200
Ru^{3+}, Bi^{3+}, Pb^{2+}, Hg^{2+}, Sb^{3+}, Pd^2, Au^{3+}	0.100
Se^{4+}, Te^{4+}, $S_2O_3^{2-}$, Zr^{4+}, V^{5+}, Th^{4+}	0.050
Ir^{4+}, Rh^{3+}, Ru^{3+}, U^{4+}	0.010
Pt^{4+}, Ag^+	0.005

*Masking with NH_4SCN.

Application: The proposed method has been successfully applied to the determination of chromium(III) in steel, biological sample and water samples.

For biological samples, an appropriate amount of samples was decomposed in a 50 mL round-bottom flask by heating with 20 mL of concentrated nitric acid and 5 mL of 30 % hydrogen peroxide on a hot plate until near dryness. A dropwise addition of concentrated hydrochloric acid was needed to obtain a colourless or yellow residue. The residue was dissolved with 5 mL of water and transferred into a 25 mL calibrated flask. The chromium contents were analyzed according to general procedure. The results are given in Table-3.

TABLE-3
DETERMINATION OF CHROMIUM IN CERTIFIED STANDARD BIOLOGICAL SAMPLES

Sample	Standard value (μg/g)	Present 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 (1.37), Cu (10.2), Fe (54), Hg (0.36), Mg (360), Mn (6.3), V (1.73), Ni (0.83), Pb (8.8)	1.40	2.5
Tea leaf (GBW08505)	As (0.191), Ba (15.7), Ca (2840), Cd (0.032), Co (0.2), Cr (1.82), Cu (16.2), Fe (373), Hg (0.004), Mg (2240), Mn (766), Ni (7.61), V (3.12), Pb (1.06), Se (0.041), Zn (38.7)	1.79	2.8

For water sample, 200 mL of water was taken and put into a 500 mL flask and concentrated to about 10 mL by heating on a hot plate. 3 mL concentrated nitric acid and 2 mL of 30 % hydrogen peroxide were added in this solution. The mixture was heated on a hot plate and evaporated to near dryness. The residue was dissolved with 8 mL water and transferred into a 25 mL calibrated flask, and analyzed s according to general procedure. The recovery of chromium was determined by adding 2.0 μg of chromium to water samples. A standard method using atomic absorption spectrometry was also used as a reference method. The results are given in Table-4.

TABLE-4
DETERMINATION OF CHROMIUM IN WATER SAMPLES

Samples	Chromium found (ng/mL)		RSD (%) (n = 5)	Recovery (%) (n = 5)
	Proposed method	AAS method		
Panlong river water	56.5	54.8	2.5	97-104
Diangci lake water	68.6	67.2	2.7	93-102
Kunming tap water	31.4	29.7	2.2	98-106

For steel, a 0.1 g amount of steel sample was previously weighed and placed in a conical flask, to which 2.0 mL of concentrated nitric acid and 1.0 mL of concentrated hydrochloric acid were added. The system was heated up to the sample was completely dissolved. The mixture was heated on a hot plate and evaporated to near dryness. The residue was dissolved with 10 mL of 2 % HCl and transferred into a 100 mL volumetric flask and the volume was filled to 100 mL with water. The chromium(III) was determined by using a proper volume of this solution according to general procedure. The results (deducted the reagents blank) were shown in Table-5.

TABLE-5
DETERMINATION OF CHROMIUM IN A CERTIFIED STANDARD LOW-ALLOY STEEL

Sample	Standard value (%)	Present method (%)	RSD (%) (n = 5
Steel (GBW01329)	C (0.188), Si (0.305), Mn (1.44), P (0.013), S (0.046), Cr (1.08), Ni (0.166), Cu (0.277), V (0.158), Ti (0.285), Al (0.112), B (0.023)	1.120	1.8
Steel (GBW08532)	C (0.506), Si (1.96), Mn (0.755), P (0.034), S (0.012), Cr (0.802), Ni (0.314), Cu (0.126), V (0.241), Ti (0.352), Al (0.201), B (0.019)	0.811	2.2

Conclusion

A comparison of the proposed methods with other spectrophotometric methods (Table-6) shows the 2-(2-quinolinylazo)-resorcin (QAR) is one of the most sensitive, selective and convenient spectrophotometric reagents for chromium(III).

TABLE-6
COMPARISON OF REAGENTS FOR SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM

Reagent	Medium/solvent	λ_{max} (nm)	ε ($\times 10^4$) L mol^{-1} cm^{-1})	Linear range (μg/mL)	Heating time (min)	Ref.
α-Benzoic oxime	Triton-X-100 medium	360	0.540	0.1-13.7	–	11
EDTA	pH 3.5-5.0	560	0.064	6.0-160	30	18
5-Br-DMPAP	pH 5.0-5.8 benzoate buffer	590	7.800	0.02-0.56	5	19
TAR	pH 5.7 CTMAB medium	545	2.730	0.05-3.0	5	22
N-Methylpiperazine-4-carbodithioate	pH range 4.5-8.2, extracted into molten naphthalene	410	0.520	6.5-65.0	30	32
QAR	pH 5.5, CTMAB medium	590	8.940	0.01-0.8	5	Present method

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