

Spectrophotometric Determination of Chromium(VI) and Total Chromium using Quercetin and Polyvinylpyrrolidone

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Summary- A spectrophotometric method for the determination of chromium(VI) and total chromium with quercetin in the absence and presence of protective colloid polyvinylpyrrolidone (PVP) has been studied. The complexes were formed in the presence of 10% v/v ethanol and acetate buffer medium at pH 5.8. Full colour development was obtained after heating the reaction mixture for 20 minutes at optimum temperature 70°C for both complexes. The corresponding molar absorptivities were 2.94×10^4 and $1.02 \times 10^5 \text{ l.mol}^{-1}.\text{cm}^{-1}$ at λ_{max} 437 nm and obeyed Beer's law within the concentration ranges 0.03-1.56 and 0.016-0.65 $\mu\text{g/ml}$ of chromium(VI) for both aqueous and sensitized complexes, respectively. The stoichiometry for both complexes was 1:2 (chromium : quercetin). The interference of most common ions was studied and some masking agents such as EDTA, H_2O_2 and oxalate were used to increase the selectivity of the method. Chromium(VI) was determined in River Nile water, industrial wastewater and drilling fluids samples. A statistical treatment of the experimental data of the proposed method has been reported.

Introduction

Several methods have been described for the spectrophotometric determination of chromium utilizing organic ligands such as phenothiazene⁽¹⁾, arsenazo III⁽²⁾, xylenol orange⁽³⁾, crystal violet⁽⁴⁾, eriochrome cyanine R⁽⁵⁾, 3,3',5,5'-tetramethyl benzidine⁽⁶⁾, bromopyrogallol red⁽⁷⁾, methylene blue⁽⁸⁾, diphenylcarbazide⁽⁹⁾, and p-amino-N,N-diethylaniline⁽¹⁰⁾.

Surfactants and protective colloids are currently used in the spectrophotometric determination of metal ions because of improving the sensitivity and selectivity of the analytical methods⁽¹¹⁻¹²⁾. Diantipyrylphenyl methane⁽¹³⁾, m-sulfoantipyrylazo⁽¹⁴⁾, 5-Br-PADAP⁽¹⁵⁾, chrome azurol S⁽¹⁶⁾, stilbazo⁽¹⁷⁾, acridine red⁽¹⁸⁾, alizarine violet⁽¹⁹⁾ and phenylfluorone and its derivatives⁽²⁰⁻²²⁾ have been used for the determination of chromium(III) and (VI) in micellar media.

Experimental

Apparatus

Measurements of absorbance were conducted on a SHIMADZU UV-VIS-NIR double beam spectrophotometer using matched quartz cells of 1-cm path length. Measurements of pH were obtained with CRISON pH-mV-meter digit model 501 Ion Analyzer equipped with a combination glass-calomel electrode. API filter press for measuring water loss of drilling fluids when applied pressure 100 ± 5 PSI through 30 minutes. High pressure-high temperature (HP-HT) filter press for measuring water loss of drilling fluids in case of deep wells when applied differential pressure 500 PSI and temperature 300°F through 30 minutes.

Reagents

All chemicals used in the proposed method were of analytical grade. Solutions were prepared with distilled or deionized water. Surfactants and protective colloids were used as received without further purification. Chromium(VI) stock solution (5×10^{-3} M) was prepared by dissolving 0.367 g of dried potassium dichromate in air oven at 140-150°C for 60 minutes. The solution was diluted to 250 ml with water in a volumetric flask. Working solutions were obtained by suitable dilution. Chromium (III) stock solution (1×10^{-3} M) was prepared by dissolving 0.200 g of chromium(III) nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water containing 2.0 ml of concentrated nitric acid and completed to 500 ml with water in a volumetric flask. Working solutions were obtained by dilution. Quercetin (3,3',4',5,7-pentahydroxyflavone) solution of 2×10^{-3} M concentration was prepared by dissolving 0.1619 g of quercetin dihydrate in ethanol and diluted to 250 ml in a volumetric flask with the same solvent. Acetate

buffer solution of pH 6.0 was prepared by adjusting the pH of 0.5 M acetic acid with dilute sodium hydroxide solution to the desired value.

Procedures

Determination of Chromium(VI) with Quercetin

Place an aliquot of the sample solution containing 0.75-39.0 μg of chromium (VI) into 25 ml volumetric flask. Add 2.5 ml of 1×10^{-3} M quercetin, 2.5 ml of ethanol and dilute with acetate buffer of pH 5.8. Heat the mixture to 70°C in water bath up to 20 minutes. Cool to room temperature and complete to the mark with the same buffer solution. Measure the absorbance at 437 nm against a reagent blank. Construct a calibration graph using a set of standards under the same conditions.

Determination of Chromium(VI) with Quercetin and PVP

Introduce an aliquot containing 0.4-17.0 μg of chromium(VI) into 25 ml of volumetric flask. Add 2.25 ml of 1×10^{-3} M quercetin reagent, 2.5 ml of ethanol, 1.25 ml of 2% w/v PVP and dilute with acetate buffer solution of pH 5.8. Heat the mixture to 70°C in water bath for 20 minutes. Cool to room temperature and complete to the mark with buffer solution. Measure the absorbance at 437 nm against an identically prepared blank. Determine the chromium(VI) concentration using a calibration graph prepared in the same way.

Determination of Total Chromium using Quercetin and PVP

Place in a beaker a solution containing not more than 16.0 μg of chromium. If chromium is present as Cr(III), it must first be oxidized to Cr(VI). If the solution contains chloride add 0.5 ml concentrated sulfuric acid, and evaporate to fumes. Cool the residue, add about 15 ml of water and 0.2 ml of 0.02 N KMnO_4 solution, cover the beaker with watch glass and heat without boiling for about 15 minutes. The acidity of the solution about 0.05-0.1 M H_2SO_4 . If the pink colour disappears, add more KMnO_4 solution dropwise. Reduce the excess of oxidant by adding 2.5% sodium azide solution dropwisely, waiting a few seconds after the addition of each drop. Avoid introducing a large excess of the reducing agent⁽²³⁾. Transfer the cooled

solution to a 25 ml standard flask, add 2.25 ml of 1×10^{-3} M quercetin solution, 2.5 ml of ethanol, 1.25 ml of 2% w/v PVP and dilute with acetate buffer solution of pH 5.8. Heat the mixture to 70°C in water bath for 20 minutes. Cool to room temperature and complete to the mark with same buffer. Measure the absorbance at 437 nm against a reagent blank. Determine the total chromium concentration using a calibration graph by the same method.

Determination of Total Chromium in Industrial Wastewater and Drilling Fluids using Quercetin and PVP

Transfer an aliquot of the sample solution containing up to 16.0 µg of total chromium into 25-ml volumetric flask. The above procedure for total chromium determination with quercetin and PVP was applied in presence of 1.0 ml EDTA of 0.1 M as masking agent.

Results and Discussion

Effect of Surfactants and Protective Colloids

The possible enhancement of the colour reaction of chromium(VI) with quercetin has been investigated by treating the binary complex with different types of surfactants and protective colloids. The utilized surfactants were: cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium bromide (CPB), cetylpyridinium chloride (CPC), benzyltrimethyltetradecyl ammonium chloride (Zephiramine) [cationic], polyoxyethylene p-tert-octylphenol (Triton X-100), ethoxylated fatty alcohol (Emulsifier S), polyoxyethylene sorbitan (Tween 20), polyoxyethylene sorbitan monopalmitate (Tween 40), polyoxyethylene sorbitan monostearate (Tween 60), polyoxyethylene sorbitan monooleate (Tween 80) [nonionic], sodium alkylbenzene sulphonate (SABS), sodium lauryl sulphate (SLS) and sodium dodecylbenzene sulphonate (SDBS) [anionic], whereas the examined protective colloids were: gum Arabic, gelatin, polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP).

A marked increase in the complex absorbance was obtained in the presence of cationic surfactants CTAB, CPB and CPC and the protective

colloids, PVA and PVP. Maximum absorbance was obtained in the presence of the protective colloid PVP. Consequently, PVP has been selected to improve the sensitivity of the complex.

Absorption Spectra The absorption spectra of the system chromium(VI)-quercetin binary complex and its reagent blank in aqueous medium in presence of 10% v/v ethanol at pH 5.5 are shown in Fig.1 (curves 1&2), respectively. The corresponding absorption maxima are 437 and 365 nm. Addition of PVP to the binary complex at optimum experimental values, the sensitized complex shows a marked increase of absorbance at the same wavelengths (curve 3), whereas, its reagent blank not affected.

Effect of pH

The influence of pH on the formation and stability of chromium(VI)-quercetin binary complex in the absence of protective colloid has been examined in the pH range 3.5-6.5. Diluted nitric acid and sodium hydroxide solutions were used for pH adjustment. Maximum pH values was obtained in the range 5.3-6.0 whereas, for sensitized complex was 5.7-6.0, utilizing different acidic buffer solutions such as, formate, acetate, succinate, phosphate and phthalate. The sensitivity of the method is slightly improved in the presence of acetate buffer solution. Therefore, acetate buffer solution of pH 5.8 was used for chromium(VI) determination in both aqueous and sensitized complexes.

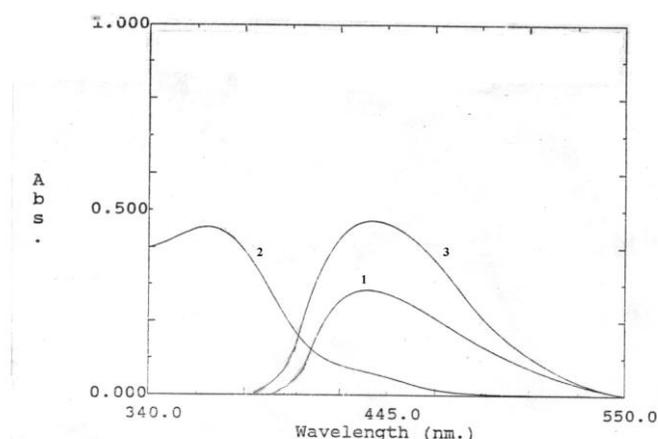


Fig.(1): Absorption spectra of Cr(VI)-Quercetin complex in absence and presence of PVP (curves 1 & 3) and their reagent blank (curve 2), respectively.

Effect of Ethanol

The effect of ethanol content on the absorbance of both aqueous and sensitized chromium(VI)–quercetin complexes was investigated at optimum experimental values. The study was conducted by preparing a series of solution containing variable amounts of ethanol ranging between 2% and 40% v/v. The results obtained indicate that, the minimum ethanol content to solubilize both complexes was 8%. Maximum colour was developed using ethanol content ranging between 8-20% and 8-25% for both aqueous and sensitized complexes, respectively. In the procedure, 10% v/v of ethanol for both complexes was used.

Effect of Quercetin Concentration

A study of the effect of quercetin concentration on the formation of the aqueous and sensitized chromium(VI) complexes were investigated using variable concentrations of quercetin ranging between 8×10^{-6} M and 1.2×10^{-4} M. Maximum colour was developed using quercetin concentration ranging between 6.8×10^{-5} M – 1.2×10^{-4} M for aqueous complex and 5.6×10^{-5} M – 1.2×10^{-4} M for sensitized complex. In the procedure, 2.5 ml and 2.25 ml of 1×10^{-3} M of quercetin were used for both aqueous and sensitized complexes, respectively.

Effect of PVP concentration

The effect of PVP concentration on the determination of the chromium-quercetin complex was studied using PVP concentration ranging between 0.008 and 0.4% w/v. The complex exerted maximum and constant absorbance in the presence of PVP concentration range 0.04-0.2% w/v. In the procedure, 1.25 ml of 2% w/v of PVP was used.

Effect of temperature

The influence of temperature on the formation of chromium(VI)-quercetin complex in the absence and presence of PVP was investigated. The applied temperature range was 30-90°C and all measurements were carried out

after 20 minute from mixing. The results obtained revealed that, the aqueous complex absorption was maximum in the range 58-75°C whereas, the enhanced complex was 63-75°C. In the procedure, the optimum temperature for both two complexes was chosen at 70°C.

Effect of time

The formation and stability of the chromium(VI)-quercetin complexes in absence and presence of PVP with respect to time were examined. The absorbance of both two complexes reaches its maximum value within 11 hours from mixing at room temperature and stable for more than two days as shown in Fig. 2 (curves 1&2), respectively. On the other hand, when the temperature was applied at the same conditions, the complexes exerted maximum absorbance through 15-25 minutes and decayed with time until reach minimum as shown in Fig.3 (curves 1&2), respectively. A standing time of 20 minutes at 70°C was used for both two complexes.

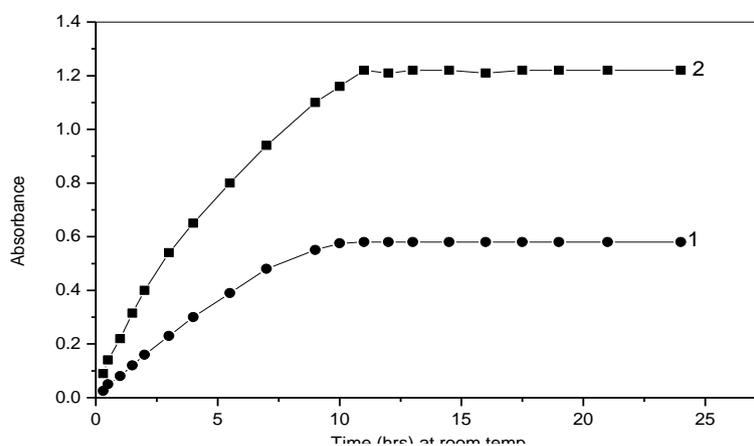


Fig.(2): Influence of time on the absorbance of chromium-quercetin complexes at room temperature. Curve 1, Cr(VI)-Qu and curve 2, Cr(VI)-Qu-PVP.

Calibration Graphs and Statistical Analysis of data

The calibration graphs of Cr(VI)-quercetin and Cr(VI)-quercetin-PVP complexes passing through the origin were linear and adhered to Beer's law in the concentration range 0.03-1.56 and 0.016-0.068 $\mu\text{g/ml}$, respectively as

shown in Fig.2. The corresponding molar absorptivities, as determined by least-squares fit for twenty five and eighteen results were 2.94×10^4 and $1.02 \times 10^5 \text{ l.mol}^{-1}.\text{cm}^{-1}$, at the same wavelength 437 nm. Moreover, the values of Sandell's sensitivity index were 1.77 and 0.51 ng.cm^{-2} of chromium(VI) and the detection limits were 0.03 and $0.01 \mu\text{g Cr(VI) ml}^{-1}$ for both aqueous and sensitized complexes, respectively.

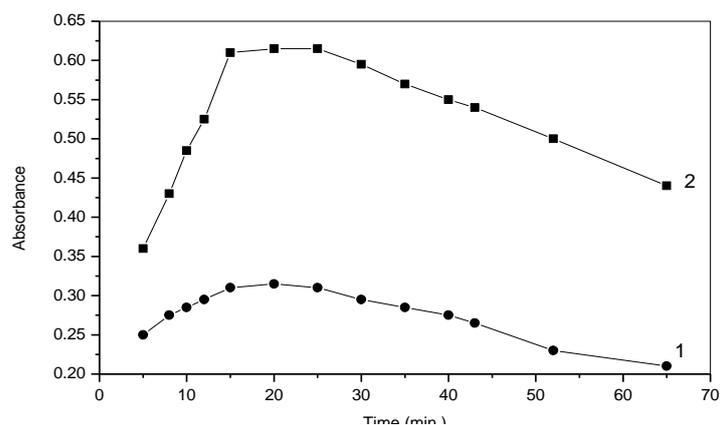


Fig.(3): Influence of time on the absorbance of chromium-quercetin complexes at 70°C.
Curve 1, Cr(VI)-Qu and curve 2, Cr(VI)-Qu-PVP.

The precision of the methods have been determined by twelve replicate of a solution containing 2.2 and 0.73 mg l^{-1} of Cr(VI), the absorbances were 0.5 and 0.46 with standard deviations of 0.009 and 0.007 , respectively. On the other hand, the corresponding values of correlation coefficients were 0.9986 and 0.9997 and the intercept on y-axis close to zero, indicating good linearity of calibration graphs and conformity to Beer's law.

Stoichiometry and Stability of the Complexes

The composition of Cr(VI)-quercetin complexes in the absence and presence of PVP at the optimum experimental values has been determined using molar ratio and continuous variation methods. The study established the existence of a binary complex with an Cr(VI)-quercetin ratio of 1:2 for both aqueous and sensitized complexes. Measurements of stability constants have

been carried out at a constant ionic strength using continuous variation method. The determined value of the stability constant for both aqueous and sensitized complexes were 3.8×10^8 and 2.8×10^9 , respectively.

Effect of Interfering Ions

The influence of foreign ions on the determination of chromium(VI) has been examined. The tolerance limit was taken as the amount that cause $\pm 2\%$ error in the absorbance value. The results obtained are given in Table 1. Some metal ions such as aluminium, iron(II) & (III), tin(II) & (IV), zirconium(IV), titanium(IV), vanadium(V), molybdenum(VI), tungsten(VI) and uranium(VI) which forms coloured complexes with quercetin seriously interfered. The selectivity of the proposed method for the determination of chromium(VI) has been improved using common masking agents such as (i) EDTA of 0.1 M for iron(II) and (III), (ii) ammonium oxalate of 0.2 M for titanium(IV), zirconium(IV) and tungsten(VI) and (iii) hydrogen peroxide of 30% for tin(II) and (IV), vanadium(V) and molybdenum(VI).

Table 1. Effect of foreign ions on the determination of chromium(VI)-Qu-PVP complex
[Cr(VI)], 2×10^{-6} M; [Qu], 9×10^{-5} M; [PVP], 0.1% w/v; pH 5.8 and T, 70°C

Ions added	Tolerance limit {[Ion]/[Cr(VI)]}
K^+ , Li^+ , Na^+ , NH_4^+ , Cl^- , Br^- , I^- , H_2O_2 , thiourea, DEA, TEA.	> 5000
SCN^- , SO_4^{2-} , $S_2O_3^{2-}$, ClO_4^- , PO_4^{3-} , formate, phthalate, succinate, Ca^{2+} , Mg^{2+} , Ba^{2+} , As^{2+} , Sr^{3+} .	> 2000
Ag^+ , B^{3+} , Bi^{3+} , $Fe(II)^a$, $Fe(III)^a$, NO_2^- , NO_3^- , F^- , thioglycolic acid, acetylacetone.	> 1000
Co^{2+} , Mn^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , tartrate, $NH_2OH \cdot HCl$.	> 500
Al^{3+b} , Pb^{2+} , Cu^{2+} , Sc^{3+} , $Sn(II\&IV)^c$, $Ti(IV)^b$, $Zr(IV)^b$, $V(V)^c$, $Mo(VI)^c$, $W(VI)^b$, malonate, sulfosalicylic acid.	>100

Masking agents:

- 1.0 ml of 0.1 M EDTA,
- 0.5 ml of 0.2 M ammonium oxalate
- 0.2 ml of 30% H_2O_2

Application of the method

The developed method utilizing chromium(VI)-quercetin-PVP system has been used to determine chromium(VI) in industrial wastewater samples.

The results obtained from wastewater of power stations, coke, electroplating baths, iron and steel, enamel and tanning industries. The results obtained are illustrated in Table 2. Moreover, the chromium(VI) concentration was measured in drilling fluids in some wells drilled in Egypt and also, the waste pits of this wells in the period from April 2000 to February 2001, as shown in Table 3. The results revealed a good agreement between the suggested spectrophotometric method and the standard method. Student t- and F-values were applied⁽²⁴⁾. The calculated t-values ranged between 1.13 – 2.45 at 95% confidence level and 5 degrees of freedom ($p = 0.05$) which lower than tabulated

(2.57). On the other hand, the F-values ranged between 1.10 – 3.30 which lower than the tabulated values at 95% confidence level (5.05) which means that, there is no difference in the precision between the proposed method and the standard method.

Table 2. Determination of total chromium in industrial wastewater using Quercetin and PVP

Sample source	Chromium, $\mu\text{g/ml}$			F-test	t-test
	AAS	*Found	RSD		
Helwan coke co.	0.03	0.027	0.08	1.34	1.72
Helwan iron and steel co.	0.04	0.04	0.07	1.10	2.02
Abu Qir power station	0.05	0.052	0.06	1.35	1.17
Shubra El-kheima p. station	0.06	0.062	0.05	2.12	1.22
Attaka power station	0.07	0.072	0.06	1.76	1.48
Abu Soltan power station	0.07	0.073	0.06	1.39	1.46
Matrouh power station	0.15	0.014	0.035	1.32	1.79
Maadi electroplating plant	0.25	0.243	0.017	1.60	1.34
Industrial union for enamel	12.8	12.805	0.02	1.43	2.78
Madbouly tanning co.	5500	5495	0.09	1.28	2.45

Table 3. Determination of chromium in drilling fluids and drilling wastes using Quercetin and PVP

Sample source / Field / Drilled well	Chromium, $\mu\text{g/ml}$			F-test	t-test
	AAS	*Found	RSD		
GPC- Shukeir- Shukier 16					
The inlet mud to the well	12.6	12.55	0.002	1.39	2.03
The outlet mud from the well	9.75	9.79	0.002	1.29	2.39
Waste pit	9.34	6.30	0.007	2.87	1.86
EBEDECO-West Bakr- M 10					
The inlet mud to the well	11.42	11.38	0.002	1.42	2.75
The outlet mud from the well	8.68	8.71	0.004	1.52	1.76
Waste pit	6.20	6.23	0.005	1.62	1.32
Petro Bel- Belaiym- Bel 113-96					
The inlet mud to the well	14.10	14.13	0.003	1.70	1.66
The outlet mud from the well	11.85	11.89	0.004	1.80	1.62
Waste pit	7.40	7.37	0.003	1.27	1.38
SUCO- Zeit Bay- ZB – B9					
The inlet mud to the well	8.68	8.91	0.005	2.81	2.33
The outlet mud from the well	6.54	6.57	0.006	2.64	1.69
Disposal in Suez Gulf	2.40	2.40	0.011	1.29	1.43
Borg El-Arab- Marina- Marina 2					
The inlet mud to the well	12.95	12.94	0.005	3.30	1.65
The outlet mud from the well	10.10	10.06	0.005	1.31	1.13
Waste pit	8.32	8.29	0.006	1.41	2.43
BAPETCO- Obayied- Obayied SW					
The inlet mud to the well	9.66	9.70	0.007	1.79	2.26
The outlet mud from the well	7.48	7.49	0.008	1.46	1.71
Waste pit	4.87	4.85	0.007	1.76	1.33

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