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2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline as an Analytical Reagent for the Spectrophotometric Determination of Microamount of Gold(III)

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The synthesis, spectral characteristics, and analytical application of 2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline (DCHNAQ) are described. A simple, rapid, selective, and sensitive spectrophotometric method for the determination of microgram amounts of gold, alone, or in the presence of associated metals, is developed, based on the color reaction between the metal ion and the reagent. The yellowish brown complex ($\lambda_{\max}$=575 nm) has stoichiometric ratio (1 : 1) [metal : ligand] over the pH range 3.4 to 7.0. Beer's law is obeyed over the concentration range 0.1—6.9 $\mu g\,cm^{-3}$ of gold. The molar absorptivity and Sandell's sensitivity of the method are 1.52×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ and 0.016 μg Au cm^{-1} respectively. The relative standard deviation for six replicate determination of 2.95 $\mu g\,cm^{-3}$ of gold(III) is 1.37%. The interference of various ions has been studied and conditions were developed for the determination of gold in alloys and some synthetic samples without the need for extraction or heating.

Gold is generally separated by the extraction of tetrachloroauric and tetrabromoauric acid using oxygen-containing solvents such as isobutyl methyl ketone (IBMK), pentyl acetate, ethyl acetate, mesityl oxide, diisopropyl ether, diethyl ether of 2,2-dichloroethyl ether, tributyl phosphate (TBP) or trioctylphosphine oxide. (TOPO) solutions in cyclohexanone. Gold may also be determined using various complexing agents such as diethyl dithiocarbamate,[1] 8-quinolinethiol,[2] 2-quinolinecarbaldehyde oxime,[3] thioacetamides,[4] aniline,[5] ethyl xanthate,[6] 2-pyridinecarbaldehvde oxime,[7] anthranilic acid,[8] di-2-thienyl ketone oxine,[9] *p*-anisaldehyde 4-phenylthiosemicarbazone,[10] propericiazine,[11] chromopyrazole,[12] phenothiazine,[13] or sodium 5-(4-sulfonatophenylazo)-8-aminoquinoline (SPAQ).[14] In most of the methods, the sensitivity is very poor and the color fades after a few minutes. In some instances the complex is formed only after heating for a long period, whereas others suffer from interferences from other metal ions. A through survey of the literature showed that no previous attempt has been made to employ 2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline (abbrev. to DCHNAQ) for the spectrophotometric determination of gold. In this work, this reagent is proposed as an analytical reagent for the rapid determination of gold. Various parameters such as pH, reagent concentration, time, temperature, and interference of foreign ions have been studied. This method has been applied to the determination of gold(III) in alloys and in certain synthetic samples. The reagent has been found to be sensitive and selective compared with other complexing agents.

Experimental

Apparatus: A Perkin Elmer Lambda 3B spectrophotometer with matched 10-mm cells in a wavelength range 190—900 nm was employed for spectral measurements and an Orion Research Model 601 A/Digital Ionalyzer pH-meter was used for checking the pH values of different buffer solutions.

Reagents: All chemicals were of analytical reagent grade (BDH Chemicals).

Synthesis of 2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline: 6-Amino-2,3-dichloroquinoxaline was prepared according to the reported method,[15] diazotized and coupled with 3-hydroxy-2-naphthoic acid. The purity and chemical structure of the azo reagent was detected by the sharp mp 324—324.5. Yield 67%. Found: C, 55.86; H, 1.83; N, 14.70; Cl, 16.84%. Calcd for $C_{19}H_{10}N_4O_3Cl_2$: C, 55.23; H, 2.44; N, 13.56; Cl, 17.16%. IR $\nu_{N=N}=1375$ cm^{-1}, $\nu_{C=O}=1625$, $\nu_{OH}=3300$, ^1H NMR (DMSO) $\delta=13.7$ (1H, d, $J=9.90$ Hz, OH), 10.3 (1H, d, $J=9.90$ Hz, COOH). So the chemical structure of this azo reagent was (Chart 1).

Color Reagent Solution: A 0.0826 g of DCHNAQ was dissolved in 100 cm^{-1} of absolute ethanol (2×10^{-3} $mol\,dm^{-3}$). A stok solution (10^{-2} $mol\,dm^{-3}$) of gold(III) was prepared by dissolving the requisite amount of pure gold(III) chloride in redistilled water and adding hydrochloric acid in order to make the solution 1 $mol\,dm^{-3}$ with respect to the acid. The solution was standardized gravimetrically by the hydroquinone method.[16]

Buffer Solutions: Buffer solutions of various pH values were prepared using 1 $mol\,dm^{-3}$ HCl – 1 $mol\,dm^{-3}$ sodium acetate (pH 1—3), 0.2 $mol\,dm^{-3}$ acetic acid – 0.2 $mol\,dm^{-3}$ sodium acetate (pH 4—7), and 0.2 $mol\,dm^{-3}$ ammonium chloride–ammonia solution (pH 8—12).

Procedures: A) Determination of Microgram Amount of Gold: A known volume of gold(III) solution not more than 172.5 μg was transferred into 25 cm^3 measuring flask. Then 10 cm^3 from acetate buffer solution of pH

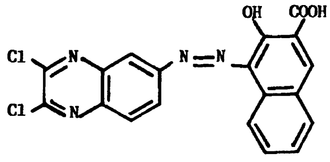

Chart 1.

5.6, 4.0 cm^3 of 2×10^{-3} mol dm^{-3} DCHNAQ reagent solution, were added to the gold(III). The mixture was diluted to the mark with redistilled water and left for about 5 min. The absorbance was measured at 575 nm against a reagent blank prepared similarly but without gold(III).

B) Determination of Gold in Gold–Copper–Silver Alloy: About 0.1 g of gold alloy was accurately weighed into a covered 50-cm^3 beaker and treated with 15 cm^3 of aqua regia. The beaker was gently heated to dissolve the alloy and then 10 cm^3 of concentrated hydrochloric acid in 2 cm^3 portions were added. The solution was evaporated to dryness on a steam bath after each addition of the acid to ensure complete removal of nitrogen oxides and excess nitric acid. The salts of the metal was dissolved in 40 cm^3 of aqueous NH_3 (sp gr 0.88), diluted with 20 cm^3 of H_2O and filtered off any insoluble residue through 542 Whatman filter paper. The solution was washed thoroughly with hot water and completed the filtrate with redistilled water to 500 cm^3.[17)] A suitable aliquot of this solution was taken in 25 cm^3 measuring flask. The solution was then treated and the absorbance was measured as in the general assay procedure. The gold content was then calculated from the calibration curve.

C) Determination of Gold in Synthetic Mixtures Corresponding to Noble Metal Dental Alloy: The recommended procedure was tested in mixture of synthetic solutions prepared in hydrochloric acid medium. The results indicated that the procedure described can be adopted in the analysis of dental alloy or any other of noble metals composition similar to that of the synthetic mixture.

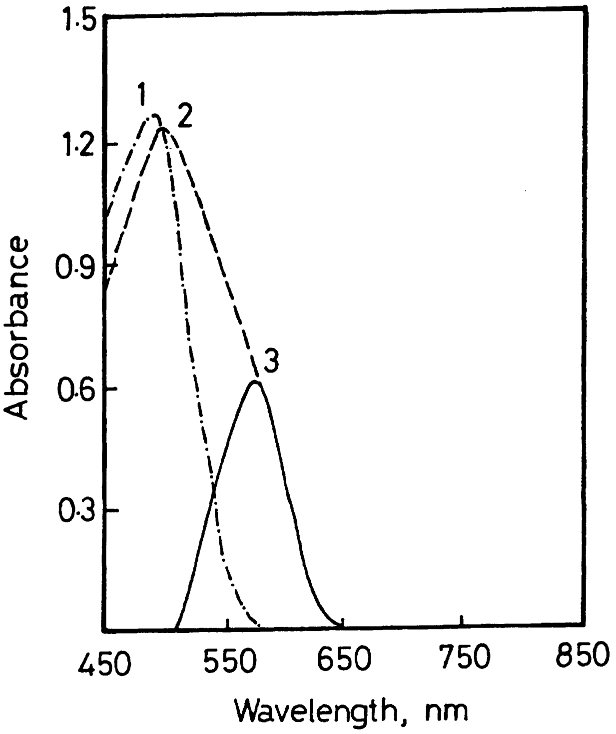

Fig. 1. Absorption spectra of DCHNAQ and its gold complex. 1: 3.2×10^{-3} M reagent, 2: 3.2×10^{-3} M reagent +74 ppm Au(III), 3: 2 against 1. (1 M=1 mol dm^{-3}).

Results and Discussion

Absorption Spectra: Absorption spectrum of DCHNAQ alone shows a maximum at 492 nm. The Au–DCHNAQ complex shows a maximum absorbance at 575 nm, where the DCHNAQ gives almost zero absorbance (Fig. 1). However, in all instances the absorbance was measured at 575 nm against a corresponding blank.

Reaction Conditions: The acid dissociation constants of DCHNAQ were obtained spectrophotometrically[18)] amounting to 3.8 (COOH) and 7.4 (OH). The log stability constant of the 1 : 1 complex as determined from the Job's method is 5.55. The optimum pH values for the Au–DCHNAQ complex is in a range 3.4—

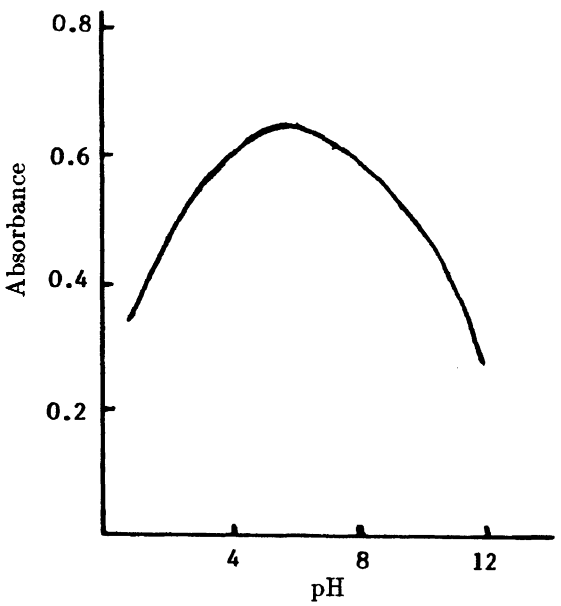

Fig. 2. Effect of pH values on the absorbance of the Au–DCHNAQ complex. [Au^{3+}] = 98.5 µg/25 cm^3 [DCHNAQ] = 3.2×10^{-4} mol dm^{-3}

Table 1. Tolerance Limits in the Determination of 74 µg of Au(III)/25 cm^3 with DCHNAQ

Ion added	Amount tolerated/µg
CH_3COO^-, Cl^-	10000
NO_3^-, $EDTA^{2-}$	5000
PO_4^{3-}, SO_4^{2-}, $B_4O_7^{4-}$	2000
Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}	1500
V^{5+}, Fe^{3+}, Cd^{2+}, Ag^+	1000
Cr^{6+}, Mo^{6+}, W^{6+}	750
Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}	500
Cr^{3+}, Ga^{3+}, Al^{3+}	300
Zr^{4+}, Ce^{4+}, Pt^{4+}	250
In^{3+}, Y^{3+}, Sc^{3+}, La^{3+}	200
Pd^{2+}, Pb^{2+}, Zn^{2+}	100
Hg^{2+}	75[a)]

a) Masked with 5 mg of EDTA.

Table 2. Determination of Gold in Egyptian Gold Alloys

Sample number	Certified composition of alloy[a] /%	Gold content of solution[b] $\mu g\,cm^{-3}$	
		Certified value	Found
1	Au, 87.66; Cu, 6.81; Ag, 6.12	1.00	0.99
		2.00	2.01
		3.00	3.02
		4.00	3.98
2	Au, 74.92; Cu, 12.53; Ag, 12.48	1.50	1.51
		3.00	3.01
		4.50	4.47
		5.50	5.47
3	Au, 55.15; Cu, 20.82; Ag, 20.82	1.25	1.26
		2.50	2.49
		3.75	3.77
		5.00	5.02

a) These values were given by Khalifa et al.[19] b) A known mass of sample was dissolved and aliquots of the solution diluted to give solutions containing four different levels of gold. The values, calculated from the gold content certified by the recommended method,[18] are expressed as certified values. The results quoted as "Found" are the mean of six determination at each concentration.

Table 3. Determination of Gold in Synthetic Mixtures Corresponding to Noble-Metal Dental Alloy

Taken/$\mu g\,cm^{-3}$						
Au	Ag	Cu	Pt	Pd	Zn	Au found[a]
$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$	$\mu g\,cm^{-3}$
2.00	0.20	0.150	0.050	0.050	0.050	2.01
3.00	0.30	0.225	0.075	0.075	0.075	3.03
4.00	0.40	0.300	0.100	0.100	0.100	3.98
5.00	0.50	0.375	0.125	0.125	0.125	5.04
6.00	0.60	0.450	0.150	0.150	0.150	5.96

a) Average of six determination.

Table 4. Comparison of Reagents for the Spectrophotometric Determination of Gold

Reagent	λ_{max} / nm	ε[a] / $dm^3\,mol^{-1}\,cm^{-1}$	Medium	Comments	Reference
Thiocaprolactam	400	3.7×10^3	$CHCl_3$	—	20
Methylene blue	657	1.8×10^5	$C_2H_2Cl_2$	—	21
Sodium azide	330	1.32×10^3	Butanol	Color stable for 15 min.	22
4,4′-Bis (dimethylamino)thiobenzophenone	540	1.2×10^5	Aqueous	30 mins requires for color development.	23
p-Anisaldehyde 4-phenylthiosemicarbazone	365	2.12×10^4	Ethylacetate	Shaking for 60 s.	10
Sodium 5-(4-sulfonatophenylazo)-8-aminoquinoline	605	1.48×10^4	Aqueous	—	14
Triisooctylamine	325	5.8×10^3	CCl_4	—	24
1-Acetyl-4-(2-pryidyl)thiosemicarbazide	460	1.5×10^4	—	—	25
Mepazine hydrochloride	514	2.18×10^4	Aqueous	Color stable for 30 min.	26
2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline	575	1.52×10^4	Aqueous	Color stable for 48 h.	This work

a) ε Molar absorptivity.

7.0 (Fig. 2), while the best one which give the highest absorbance and most stable complex at pH=5.6, thus confirming that the mono anionic species are the reactive ones. Maximum and stable absorbance is attained with 2.0—5.0 cm^3 of 2×10^{-3} $mol\,dm^{-3}$ DCHNAQ solution, and the use of 4.0 cm^3 is selected as optimal.

At room temperature, the maximum absorbance is obtained 5 min. after the mixing the components, and is stable for two days at least. Raising the temperature up to 55 °C has no effect on the formation of the complex, above which the absorbance of the complex starts to decay and the band will disappears during boiling of the mixture. The order of mixing of reagents seriously affects the absorbance value, however, addition in the order Au(III), buffer and DCHNAQ gives the best results.

Analytical Characteristics: A calibration graph was constructed under the optimum conditions described above. The system obeys Beer's law over the concentration range 0—172.5 µg of gold(III) in 25 cm^3 of final solution. For more accurate results Ringbom's optimum concentration ranges was 2.5—157.5 µg/25 cm^3. The molar absorptivity and Sandell's sensitivity of the method are 1.52×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ and 0.016 µg Au cm^{-1} respectively. The relative standard deviation for six repeated determinations of 2.95 $\mu g\,cm^{-3}$ of gold(III) was 1.37%.

Interference: The influence of 36 kinds of ions on the determination was examines. The ions tested were added individually to a solution containing 74 µg of gold(III). A maximum error of 2% in the absorbance reading was considered tolerable. The tolerance limit of foreign ions is given inTable 1. The interference from Hg^{2+} was eliminated by masking with EDTA. Thus the data in Table 1 indicate the reasonable selectivity of the method in the presence of associated ions.

Applications: In order to confirm the usefulness of the proposed spectrophotometric method, it has been applied to the determination of gold(III) in gold–copper–silver alloy (Table 2) and in synthetic mixtures corresponding to noble-metal dental alloy, (Table 3).

Conclusion

The comparison (in Table 4) of the DCHNAQ method with others shows that the proposed method for spectrophotometric determination of gold is sensitive, selective, simple, and rapid, it does not require heating or extraction with organic solvents, and may be used to determine microamounts of gold in small samples directly in aqueous solution.

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