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SYNTHESIS AND CHARACTERIZATION OF 1,2-CYCLOHEXANEDIONE BIS-BENZOYLHYDRAZONE AND ITS APPLICATION TO THE DETERMINATION OF Ti IN MINERALS AND ROCKS

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Summary—The synthesis, spectroscopic characteristics and analytical applications of 1,2-cyclohexanedione bis-benzoylhydrazone are reported. The reaction of this new compound with titanium(IV) has been studied spectrophotometrically. An orange 1:2 metal/ligand complex ($\lambda_{max} = 477$ nm, $\epsilon = 1.05 \times 10^4$ l.mole^{-1}.cm^{-1}) is formed at pH 1.75–3.0 in 3:2 v/v ethanol–water medium. The method is simple and selective and has been satisfactorily applied to the determination of titanium in bauxite, Portland cement, amphibolites and granites.

Aroylhydrazones have been mainly used as chromogenic reagents for the determination of metal ions.[1–6] Bis-aroylhydrazones have also been used as analytical reagents, particularly those derived from oxalyldihydrazone.[1] Lever[7] has reported the spectrophotometric and fluorimetric properties of the bis-(4-hydroxybenzoylhydrazone) derivatives of glyoxal, methylglyoxal and dimethylglyoxal, the glyoxal derivative being used for the colorimetric determination of calcium and cadmium. Zinc has been determined gravimetrically with the bis(2-hydroxybenzoylhydrazone) and bis-(5-bromo-2-hydroxybenzoylhydrazone) of dimethylglyoxal.[8] The analytical properties of diphenylglyoxal and dipyridylglyoxal bis(2-hydroxybenzoylhydrazone)[9–12] and bis-benzoylhydrazone[13] have also been investigated. Less attention has been paid to the use of bis-aroylhydrazones derived from cyclic ketones.

In the present paper, the synthesis, properties and analytical applications of 1,2-cyclohexanedione bis-benzoylhydrazone (CHBBH) are reported. A rapid and simple method for the colorimetric determination of titanium has been developed and applied to the determination of this element in mineral and siliceous materials.

EXPERIMENTAL

Reagents

Salts and solvents of analytical-reagent grade purity or better were used throughout and all solutions were prepared with distilled demineralized water.

CHBBH solutions, 0.2, 0.1, 0.05 and 0.0375% in ethanol, 0.1 and 0.05% in dimethylformamide and 0.05% in chloroform, were prepared.

A stock titanium(IV) solution (Ti 1.046 g/l.) was prepared by dissolving titanium metal in 4*M* hydrochloric acid and oxidizing with concentrated nitric acid, and standardized gravimetrically with cupferron.[14] Working solutions of the required concentration were prepared daily from this solution.

Buffer solution of pH 2.4 was made by dissolving 94.5 g of monochloroacetic acid and 16.2 g of sodium hydroxide in water and diluting to 1 litre. Other buffer solutions (phthalate, acetate and ammonia) were prepared by conventional methods.

Preparation of the reagent

The reagent was synthesized by the general procedure for related compounds.[5,6] Benzoylhydrazide, 1 g in 14 ml of ethanol, was mixed with 0.41 g of cyclohexanedione in 15 ml of ethanol, several drops of concentrated hydrochloric acid were added and the mixture was refluxed for 30 min.

The white crystals (tetragonal symmetry, $a = b =$ 15.78 Å, $c = 19.82$ Å) produced were filtered off, washed, recrystallized from ethanol and dried at 100°. Yield 60%; melting point 209°.

Elemental analysis gave C 68.7%, H 5.8%, N 16.3%. $C_{20}H_{20}N_4O_2$ requires C 68.98%, H 5.74%, N 16.09%.

The reagent is thermally stable in air up to the melting point, as deduced from data obtained by thermogravimetry and differential thermal analysis.

Spectrophotometric procedures

Ionization constant. Determined by the Stenström and Goldsmith[15] and Phillips and Merritt[16] methods by measuring the absorbance at 325 and 360 nm against water, for solutions adjusted to various pH values.

Determination of titanium. In a 25-ml standard flask, place a suitable volume of sample solution containing up to 100 μg of Ti(IV), 15 ml of 0.05% CHBBH solution in ethanol, 5 ml of monochloroacetate buffer and dilute with water to the mark. After 5–10 min measure the absorbance at 477 nm against water.

Prepare a calibration graph by using standard titanium solutions treated in the same way.

Decomposition of samples

Amphibolites and granite. Dry the sample at 110°, weigh accurately 0.5–1 g in a platinum crucible, add a 6-fold weight of lithium metaborate and fuse at 1000° for 2 hr. Cool, extract the melt with 2*M* hydrochloric acid and remove the silica precipitate, collecting the filtrate in a 500-ml standard flask and making up to volume with dilute hydrochloric acid. Use a 1–4 ml portion for the determination of titanium.

Portland cement. Weigh accurately *ca.* 1 g of sample (dried at 110°) into a beaker and dissolve it in hydrochloric

Table 1. Ultraviolet spectra of CHBBH in some common solvents

Solvent	D*	λ_{max}, nm	ϵ, l.mole^{-1}.cm^{-1}	λ_{max}, nm	ϵ, l.mole^{-1}.cm^{-1}
Dimethylformamide	37.6	335	1.06×10^4	277	8.69×10^3
Methanol	32.63	329	1.13×10^4	266	1.20×10^4
Ethanol	24.3	328	1.13×10^4	265	1.14×10^4
Acetone	20.7	335	1.02×10^4	—	—
3-Methylbutan-l-ol	14.7	335	1.13×10^4	—	—
n-Pentanol	13.9	334	1.14×10^4	273	1.14×10^4
Isobutyl methyl ketone	13.11	340	1.02×10^4	—	—

*D = dielectric constant at 25°.

acid, evaporate to dryness, digest with 6*M* hydrochloric acid and filter off the silica precipitate. Dilute the filtrate to volume with water in a 500-ml standard flask. Use a 3 or 4 ml portion for the determination.

Bauxite. Weigh about 1 g of sample into a Kjeldahl flask, heat for 60 min with a mixture of concentrated sulphuric, nitric and hydrochloric acids (1:1:1 v/v), evaporate to fumes of sulphuric acid, leach with dilute hydrochloric acid and filter. Fuse the residue with potassium pyrosulphate and extract the cooled melt with dilute hydrochloric acid and filter. Combine the filtrates in a 500-ml standard flask and make up to the mark with water. Take a 1 or 2 ml portion for the determination.

In all instances, add 0.2 ml of thioglycollic acid to avoid possible interferences.

RESULTS AND DISCUSSION

Analytical properties of the reagent

The wavenumber of the C=O band of aroylhydrazones in the infrared spectrum has already been reported.[17-20] The absorption bands associated with the imine group are also well known.[21,22] The bands at 3220 and 3170 cm^{-1} can be attributed to the N—H stretching vibration for associated secondary amines.[23] Amide I (1655 cm^{-1}, very strong), amide II (1510 cm^{-1}, medium) and amide III (1270 cm^{-1}, strong) bands are assigned in agreement with the observations made by Domiano *et al.*[18] and Pelizzi and co-workers.[19,20]

Table 1 shows the spectral characteristics of the reagent ($1.15 \times 10^{-4}M$ solution) in some common organic solvents. The reagent shows two maxima (at 265–280 and 335–340 nm), except in acetone, 3-methylbutan-l-ol and isobutyl methyl ketone. The absorption spectrum shows a slight red-shift as the polarity of the solvent decreases. The main absorption band is probably due to an $n \rightarrow \pi^*$ transition.[18]

In 4% ethanol–water medium CHBBH is pale yellow in acidic or neutral media, and bright yellow in alkaline solution. The spectra are shown in Fig. 1. The red shift from 330 to 345 nm in basic media (curves 4 and 5) is due to formation of anionic species of the type $>C{=}N{-}N{-}C{<}O^-$. The blue shift from 265 to 245 nm in acid medium (curve 1) is attributed to protonation of a nitrogen atom in the hydrazide group and to hydrolysis of the reagent to yield its parent species. The dissociation constant for the proton of the —CONH— group, was evaluated by the Phillips and Merritt[16] and Stenström and Goldsmith[15] methods. The value found was 10.4 ± 0.1, in agreement with those obtained for related aroylhydrazones.[13,24] Solutions of the reagent in ethanol, dimethylformamide, methanol, acetone

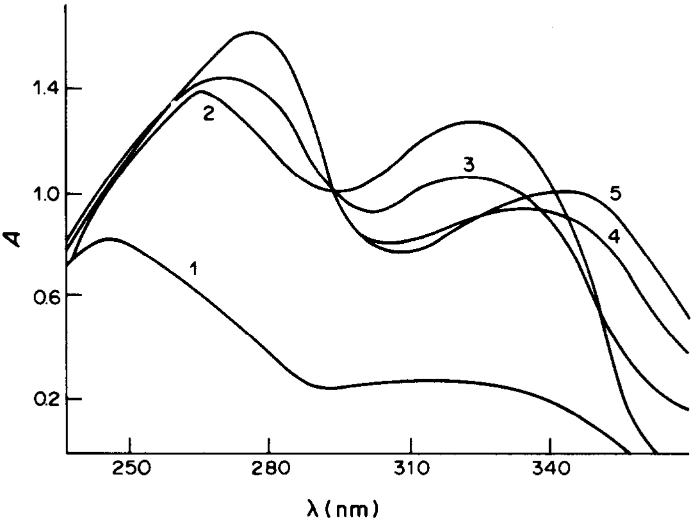

Fig. 1. Absorption spectra of CHBBH ($1.15 \times 10^{-4}M$) in 4% aqueous ethanol medium at different pH values: 1, pH = 2.34; 2, pH = 4.23; 3, pH = 9.88; 4, pH = 11.30; and 5, pH = 12.83.

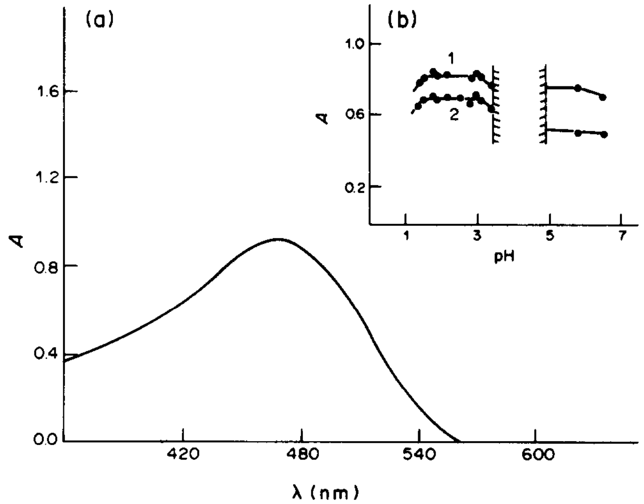

Fig. 2. (a) Absorption spectrum of the Ti(IV)–CHBBH chelate in 60% aqueous ethanol at pH 2.4 (titanium concentration 4.18 μg/ml). (b) pH–absorbance graph of the chelate at (1) 477 nm, and (2) 500 nm (the pH values between parallel segments correspond to a region where precipitation occurs).

and n-pentanol are stable for at least a month, whereas the reagent decomposes in 3-methylbutan-l-ol and isobutyl methyl ketone. In acid aqueous solution, CHBBH is rapidly hydrolysed, but in moderately strong basic media no hydrolysis takes place. However, the hydrolysis is less severe in aqueous ethanol as the proportion of ethanol is increased.

Reducing substances, such as thiosulphate, ascorbic acid and hydroxylamine, do not affect the rate of hydrolysis of the reagent in aqueous ethanol solution, but sulphite appears to stabilize the reagent in moderately strong acid medium. Persulphate and hydrogen peroxide have no effect on the reagent at low pH, but hydrogen peroxide decomposes it in basic media.

A systematic study of the reaction of CHBBH with 40 different ions showed that the most interesting metal complexes were formed in chloroacetate buffer (pH 2.4), acetate buffer (pH 4.5) or ammonia buffer (pH 9.5) with Fe(III), Fe(II), Ti(IV), Pd(II), V(V), Sb(III), W(VI), Mo(VI), Cu(II) and Bi(III). The presence of at least 40% v/v ethanol is necessary to prevent the precipitation of the metal chelate or excess of reagent. Once formed, the chelates are all readily extracted into chloroform but when the metal ion solutions are shaken with a chloroform solution of the reagent only the Cu(II), Mo(VI), Bi(III) and Sb(III) complexes are extracted.

Spectrophotometric study of the Ti(IV)–CHBBH system

Formation of the Ti(IV) chelate. An aqueous Ti(IV) solution reacts with an ethanolic solution of CHBBH in acidic medium (optimum pH value 1.8–3.0) to form an orange chelate that shows excellent analytical properties. The spectrum shows an absorption maximum at 477 nm, where the reagent does not absorb (Fig. 2). The titanium chelate is completely

Table 2. Tolerance limits in the determination of 45 μg/25 ml of Ti(IV) with CHBBH

Ion*	Tolerance limit, *mg/25 ml*
Ba^{2+}, Na^{+}, Tl(I), Hg(I), ascorbic acid, H_3BO_3, Cl^{-}, NO_3^{-}, Ni^{2+}	50
Mg^{2+}, Sr^{2+}†, Cs^{+}†, Br^{-}, ClO_3^{-}, $S_2O_3^{2-}$, acetate	40
Benzoate	30
Ca(II), Ag(I), Rb(I)†, SCN^{-}, $B_4O_7^{2-}$	25
La(III), Li(I), Zn(II), Hg(II), Pb(II), As(III), ClO_4^{-}	20
S^{2-}	10
Al(III), $Fe(CN)_6^{3-}$, tartrate	5
Th(IV), $Cr_2O_7^{2-}$, BrO_3^{-}, NO_2^{-}, CrO_4^{2-}, CO_3^{2-}, SO_2^{2-}, citrate	2.5
Co(II), Cd(II), SiO_3^{2-}, NH_4^{+}, MnO_4^{-}	1.5
Cu(II)	0.5
H_2O_2, AsO_4^{3-}, In(III)	0.3
Sb(III)	0.2

*Cations were added in the form of chlorides or nitrates; anions were added in the form of sodium or potassium salts.

†Maximum concentration tested. The mean value for eleven samples with 2 μg/ml Ti gave a relative error of 0.3% for a probability level of 95% ($P = 0.05$).

Table 3. Tolerance limits of foreign ions in the presence of masking agents

Ion	Tolerance limit* *μg/ml*	Masking agent†
Al(III)	600	Tiron (1000 μg/ml)
Al(III)	600	Tartaric acid (200 μg/ml)
Mo(VI)	20	
Ce(III]	10	
Sb(III)	6	
Fe(III), Pd(II)	2	
Ag(I), Hg(II)	1200	Thiourea (4000 μg/ml)
Cu(II)	100	
Ag(I), Zn(II), Hg(II)	1000	Thiocyanate (1000 μg/ml)
W(VI)	10	
Ag(I), Hg(II)	1200	Sulphide (400 μg/ml)
As(III)	800	
Cu(II)	80	
Bi(III)	60	
Sb(III)	12	
Cu(II), Hg(II), Pb(II)	1600	Thioglycollic acid (4000 μg/ml)
Bi(III)	100	
Sn(IV)	80	
Sn(II), Fe(III)	60	
Pb(II)	1000	Thiosulphate (1000 μg/ml)
Co(II)	120	
Cu(II)	100	
Fe(II)	30	
Bi(III), Fe(III), Pd(II)	10	
Fe(CN)$_6^{4-}$	200	Zn(II) (800 μg/ml)
F$^-$	80	La(III) (800 μg/ml)
F$^-$	10	H_3BO_3 (5000 μg/ml)
SO$_4^{2-}$, PO$_4^{3-}$, SO$_3^{2-}$, CO$_3^{2-}$	2000	Ba(II)
Mn(II)	20	Peroxydisulphate (crystals) + Ag(I)
Pd(II)	100	DMG§ (1000 μg/ml)
Zr(IV)	100	Periodate (0.5 g)

*If a precipitate is formed, filter or centrifuge before measuring absorbance.

†The amount added is shown in parenthesis.

§DMG: dimethylglyoxime.

Table 4. Comparative determination of Ti in rocks and siliceous materials by the CHBBH and AAS methods

	Ti, %		
	CHBBH method		
Sample	Present procedure*	SAM†	AAS§
Amphibolite (A-63)	0.81 ± 0.01	0.80 ± 0.03	0.75
Amphibolite (A1512)	0.94 ± 0.02	1.01 ± 0.05	0.98
Amphibolite (A-1618)	0.264 ± 0.04	0.30 ± 0.01	0.25
Granite (G-3)	0.12 ± 0.01	0.11 ± 0.02	0.10
Granite (G-8)	0.44 ± 0.01	0.50 ± 0.03	0.46
Portland cement (BCS, No. 372)	0.34 ± 0.02‡	0.32 ± 0.03‡	0.33‖
Bauxite (BAS, No. 87)	2.24 ± 0.03‡	2.28 ± 0.04‡	2.25‖

*Mean value and range of duplicate analyses corresponding to two different weights of every sample, with two aliquots of different volume from each sample solution.

†SAM: standard addition method.

§Quadruplicate determinations by atomic-absorption spectroscopy. Since the sensitivity is lower than that of the CHBBH-based method, a larger sample is needed.

‡Given as percentage of TiO_2.

‖Certified value as percentage of TiO_2.

Table 5. Comparison between the spectrophotometric determination of titanium by the CHBBH method and other methods

Reagent	Optimal acidity	λ_{max}, *nm*	ϵ, *l.mole*$^{-1}$.*cm*$^{-1}$	Interfering ions[a]	Ref.
Hydrogen peroxide	H_2SO_4	410	0.7×10^3	Fe^{3+}, F^-, $C_2O_4^{2-}$, Mo(VI), V(V), U(VI), citrate	26
Benzohydroxamic acid	5*M* HCl	370	2.4×10^3	Ce(IV), V(V), Mo(VI), W(VI), Fe^{3+}	27, 28
Chromotropic acid	pH 2.7–4.6	410	1.15×10^4	Fe^{3+}, Zr(IV), F^-, oxidants	29
Tiron	pH 4.3–9.6	390	1.59×10^4	Fe^{3+}, U(VI), Mo(VI), Zr(IV), Al^{3+}, Cu^{2+}, V(V), rare earths	30
Aesculatin	pH 5.5	420	—	Be^{2+}, Ni^{2+}, Th(IV), Cu^{2+}, Ce(IV), Zr(IV), Mo(VI), Fe^{3+}, Fe^{2+}	31
N-Benzoyl-*N*-phenylhydroxylamine	pH 1.7–1.85	340	5.0×10^3	Fe^{3+}, V(V), Mo(VI)	32
Phenylfluorone	pH 9–10	460	—	Fe^{2+}, Zr(IV), V(V), Cr(VI), W(VI), Mo(VI), Nb(V), Ta(V)	33
Calcichrome	pH 4.2	565	1.15×10^4	Fe^{3+}, Al^{3+}, Cu^{2+}, Ni^{2+} V(V), Zr(IV)	34
Chrome Azurol S	pH 3.2	570	—	Al^{3+}, Fe^{3+}, Cu^{2+}, W(VI), Cr(VI)	35
Kaempferol	—	425	5.4×10^3	Zr(IV), U(VI), Mo(VI), Th(IV), Sc^{3+}, Be^{2+}, Al^{3+}, Fe^{3+}, lanthanides	36
Sulphosalicylic acid	pH 3.2–4.9	445	8×10^3	Al^{3+}, Ni^{2+}, Mo(VI), Fe^{3+}, Zr(IV)	37
Fast Grey R.A.	0.002*M* HNO_3	554	1.2×10^4	Fe^{3+}, V(V), Zr(IV), Cu^{2+}, Ga^{3+}, F^-, Cd^{2+}, W(VI)	38
Catechol Violet	pH 3.3–3.5	690	5.5×10^4	Zr(IV), Sb^{3+}, Ga^{3+}, In^{3+}, Al^{3+}, Pb^{2+}, Ce(IV), W(VI)	39
Adrenaline	Conc. H_2SO_4	500	1.7×10^3	Ta(V), Nb(V), W(VI), Mo(VI), Al^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, V(V)	40
Pyridoxal salicyloylhydrazone	pH 0.9–2.5	390 440	5.5×10^3 3.9×10^3	Mo(VI), W(VI), Cr^{3+}, F^- (at 390 nm)	3
Diphenylglyoxal bisbenzoylhydrazone	pH 4.7	520	810	Not studied	13
Dipyridylglyoxal bisbenzoylhydrazone	pH 4.7	395 470	8.9×10^3 2.4×10^3	Not studied	13
Salicylaldehyde 2-methylisonicotinoylhydrazone	pH 1.8–3.8	425	4.44×10^4		41
1,2-Cyclohexanedione bisbenzoylhydrazone	pH 1.8–3.0	477	1.05×10^4	See Tables 2 and 3	This work

[a] Ions interfering when present at the same concentration level as titanium.

formed within 5 min of mixing the reagents and remains stable for at least 2 hr.

To find the conditions needed (*a*) to avoid precipitation of the metal chelate and reagent excess, (*b*) to decrease the rate of hydrolysis of the reagent, and (*c*) to increase the sensitivity of the reaction, the influence of the organic solvent/water ratio (ethanol/water and DMF/water from 1:4 to 3:2 v/v, and ethanol/DMF/water 2:1:2 v/v), the choice of buffer solution (phthalate and chloroacetate) and the amount of reagent solution (1–14 ml of 0.2% solution in ethanol) was examined. The optimal conditions found were a medium containing 60% v/v ethanol, 2–12 ml of 0.2% reagent solution, and chloroacetate buffer. The ionic strength of the solution and the order of addition of the reagents are immaterial.

The continuous-variations method showed the formation of two complexes, with metal/ligand ratios of 1:1 and 1:2. The 1:1 complex is not observed when the absorbance measurements are made more than 2 hr after preparation of the samples. The Asmus method[25] also gave the 1:1 ratio and a new ratio of 2:3, possibly from averaging of the 1:1 and 1:2 ratios. The charge on the Ti(IV) complex and the reagent was investigated by anion-exchange, and it was concluded that the complex is positively charged, but the reagent is neutral.

Spectrophotometric determination of titanium

Under the optimum conditions for formation of the titanium complex, the absorbances at 477, 490 and 500 nm are all linearly related to the titanium concentration over the range 0.25–8.25 μg/ml.

A systematic study of interferences in the determination of 1.8 μg/ml Ti(IV) (Table 2) showed that Bi(III), Fe(III), Mo(VI), Sn(II), V(V) and Zr(IV) interfere when present at the same concentration level as Ti(IV), but Fe(II), Mn(II), Pd(II), Sn(IV), U(VI), W(VI), Fe(CN)$_6^{4-}$, F$^-$ and PO$_4^{3-}$ interfere at greater concentration. The tolerance limits for most interfering species can be increased by addition of masking agents (Table 3) and this enlarges the scope of the CHBBH system for practical determination of titanium.

Determination of titanium in bauxite and siliceous materials

The proposed method was satisfactorily applied to the determination of titanium in two standard samples (bauxite and Portland cement) and several rocks (amphibolites and granites). Table 4 summarizes the results obtained. Those for the rock analysis are compared with those obtained by atomic-absorption spectrometry. The method of standard additions was also used for validation.

CONCLUSION

The proposed procedure compares satisfactorily with other methods proposed for the spectrophotometric determination of titanium(IV) (Table 5). The method is relatively free from interferences because most metal chelates of CHBBH are not completely formed in moderately strongly acidic media, and their absorption maxima occur at wavelengths shorter than 435 nm; the selectivity is increased by the addition of suitable masking agents.

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