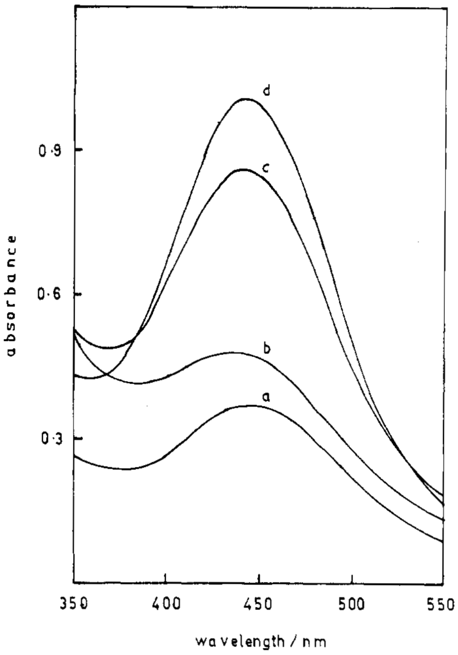

Figure 2. Absorption spectra of the colored product of acetaminophen in water (a) and in 40% acetone (d) and of aspirin in water (b) and in 40% acetone (c).

trans acetylate 4-aminophenol. The only interfering substance is acetaminophen and it should be predetermined.

Registry No. Aspirin, 50-78-2; 4-aminophenol, 123-30-8; acetaminophen, 103-90-2.

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RECEIVED for review August 26, 1985. Accepted November 4, 1985. Thanks are due to University Grants Commission, New Delhi, for a Junior Research Fellowship to A.J.

Spectrophotometric Determination of Iron in Wines, Foods, and Minerals with 5,5-Dimethyl-1,2,3-cyclohexanetrione 1,2-Dioxime 3-Thiosemicarbazone

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A new reagent, 5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime 3-thiosemicarbazone, has been synthesized and studied spectrophotometrically and a simple, rapid, selective, and sensitive method for the spectrophotometric determination of iron has been developed based upon the formation of (5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime 3-thiosemicarbazone)–iron(II) complex. A violet color is formed in strongly acid medium and the absorbance is measured at 550 nm. The molar absorptivity is 8.9 × 10^3 L·mol^{-1}·cm^{-1} and the relative error is 0.5% (3 ppm of iron). The detection limit is 0.05 μg·mL^{-1} of Fe(II) and the determination limit is 0.1 μg·mL^{-1} of Fe(II). The method has been applied to the determination of iron in wines, minerals, and foods.

Thiosemicarbazones have been widely used for spectrophotometric determination of inorganic ions and their analytical applications have been reviewed (*1–3*). Thiosemicarbazones of greatest analytical interest are those that posses another complexing group. The most important of these are the *N*-pyridine, the oxime group, and the phenolic group, in adjacent position to the thiocarbonyl group. The other complexing group can be other thosemicarbazonic group. In this paper, the analytical properties and applications of 5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime 3-thiosemicarbazone (DCDT) are presented.

An important section of this paper is the development of a method of determination of iron in wine. The determination

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of iron in wines is a requisite routine plant control analysis. Procedures usually used for the determination of iron in wine involve "wet ashing" in the preparation of the sample for analysis. All organic matter of the wine sample should be oxidized and removed by this process. Two reaction techniques have been commonly applied in this preparation procedure. First, the nitric–perchloric acid digestion. Second, the hydrogen peroxide oxidation. In the present paper a method for determination of iron in wine is developed without the requisite wet ashing accompanying procedure in the preparation of the sample for analysis. From bibliographic data, it is deduced that other methods without this previous requisite need an ion-exchange or extraction procedure. This "in situ" procedure is thus more direct and time saving with procedural simplification and with no loss of specificity or sensitivity. Another usually used procedure for the determination of iron in wine, atomic absorption spectrophotometry, needs the preparation of standards with amounts of ethanol and water similar to that of the sample.

EXPERIMENTAL SECTION

Apparatus. Beckman Model 25 and Zeiss DMR 11 spectrophotometers with 1.0 cm path length glass or quartz cells and a Crison digit 74 pHmeter with a combined SCE–glass electrode were used.

Reagents. All chemicals were of analytical reagent grade or better. Stock standard Fe(III) and Fe(II) solutions (1.984 g·L^{-1} and 1.002 g·L^{-1}, respectively) were standardized, the former gravimetrically and the latter by titration with $K_2Cr_2O_7$. All subsequent iron solutions were prepared by dilution. Solutions of DCDT in dimethylformamide of various concentrations were used by dissolving solid reagent samples prepared and purified by the authors.

Synthesis of DCDT. To obtain the DCDT, 5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime was previously obtained by Haas's procedure (*4*) modified by the authors. Two grams of powdered 5,5-dimethyl-1,3-cyclohexanedione was dissolved in a solution of 10 g of potassium hydroxide in 30 mL of water; 30 mL of ethanol was then added and, while the solution was cooled in a freezing mixture and throughly stirred, 1.2 g of KNO_2 was added and the solution was neutralized with concentrated HCl until slight excess. This solution, even cold, was mixed with a solution of 1.0 g of hydroxylamine hydrochloride in water and sodium acetate was added until a pH value of 5 was obtained. The white precipitate obtained was filtered and washed with water (yield 70%). To synthesize the DCDT, a solution of 1.24 g of thiosemicarbazide in 50 mL of water and 100 mL of ethanol was added to a solution of 2.5 g of 5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime in ethanol. The solution was stored for 3 or 4 days and the solvent then removed at 30 °C under diminished pressure. A yellow solid is separated and recrystallized in ethanol–water (mp 183–185 °C; yield > 50%). Anal. Calcd for $C_9H_{15}N_5O_2S$: C, 42.02; H, 5.84, N, 27.24. Found: C, 41.54; H, 5.89; N, 26.74. A potentiometric titration confirms the purity of obtained product.

Recommended Procedure for the Determination of Iron. Into a 25-mL volumetric flask, a suitable aliquot of sample solution containing up to 150 μg of iron, 3 mL of concentrated HCl, and 1 mL of 1% reagent solutions in DMF were transferred, diluted to the mark with deionized water, and mixed well. The absorbance was measured at 550 nm by using a 1.0-cm cell against deionized water. A suitable prepared calibration graph or empirical calculation was used to convert absorbance into concentration.

Determination of Iron in Wines. Into a 25-mL volumetric flask, a suitable aliquot of wine containing between 2.5 and 150 μg of iron, 3 mL of concentrated HCl, and 1 mL of 1% reagent solution in DMF were transferred, diluted with deionized water, and mixed well. The absorbance was measured at 550 nm against a blank of wine with 3 mL of concentrated HCl, if measurable color was present.

Determination of Iron in Vegetables and Verdures. The method has been applied to determination of iron in spinach and lentils. About 20 g of spinach, after being dried at 110 °C, was calcined and treated, heating, with 10 mL of concentrated HCl. The solution was filtered and carefully washed into a 100-mL volumetric flask. Aliquots of 5 mL were used in the spectrophotometric determination of iron with DCDT by the recommended procedure. To determine iron in lentils, about 20 g of sample was calcined and treated, heating, with 10 mL of concentrated HCl. The solution was filtered and carefully washed into a 100-mL volumetric flask and aliquots of 1 mL were used in the spectrophotometric determination of iron.

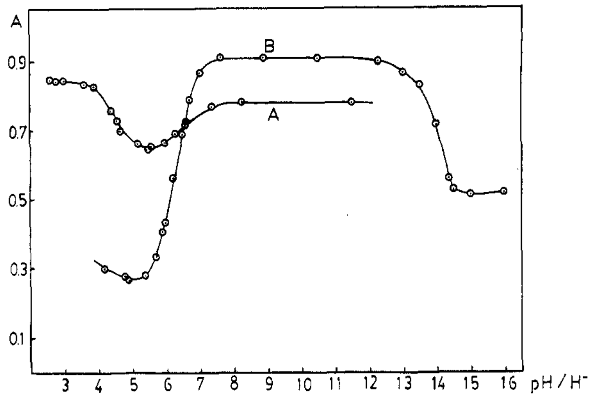

Figure 1. Ionization constant calculation: (A) [R] = 7.78×10^{-5} M, λ = 315 nm; (B) [R] = 3.89×10^{-5} M, λ = 285 nm.

Determination of Iron in Magnesites. About 0.5 g of sample was treated with 10 mL of concentrated HCl, the mixture was heated, and the solution was filtered and carefully washed into a 100-mL volumetric flask, in the event of high-purity magnesite, or into a 500-mL volumetric flask in the event of magnesite–chrome. Aliquots of 5 and 1.5 mL were used, respectively, in the spectrophotometric determination of iron with DCDT by the recommended procedure.

Determination of Iron in Portland Cement. About 0.25 g of sample was mixed with 0.5 g of NH_4Cl and treated with 5 mL of concentrated HCl, and the mixture was heated in a water bath for 30 min. Twenty milliliters of hot water was added and the solution was filtered and carefully washed into a 100-mL volumetric flask. Aliquots of 1 mL were used in the spectrophotometric determination of iron.

RESULTS AND DISCUSSION

Analytical Properties of 5,5-Dimethyl-1,2,3-cyclohexanetrione 1,2-Dioxime 3-Thiosemicarbazone. Solubility. The solubility of DCDT in several solvents at room temperature was determined by Wittemberger's method (*5*). DCDT is very soluble in DMF (73.2 g·L^{-1}), moderately soluble in ethanol (14.5 g·L^{-1}), isoamyl alcohol (6.2 g·L^{-1}), and methyl isobutyl ketone (6.8 g·L^{-1}), and sparingly soluble in chloroform (0.6 g·L^{-1}) and water (0.2 g·L^{-1}).

Stability. Solutions of 3.8×10^{-3} M reagent in dimethylformamide are not very stable. It is advisable to prepare these every day. The stability of dilute aqueous solutions (3.8×10^{-5} M) is smaller at $3 < pH < 8$.

Spectral Characteristics. The infrared spectrum was obtained (KBr disks) and the bands were assigned (cm^{-1}) to the stretching vibrations of C=N–OH (3420), –NH– (3280), –OH (3140), C=N– (1590), and C=S (1130). The ultraviolet absorption spectra in water show a maximum at 310 nm in acid medium and a maximum at 285 nm in neutral or basic medium.

Ionization Constants. The ionization constants were determined by the Stenstrom and Goldsmith method (*6*) at 20 °C and ionic strength 0.1. The results obtained were $pK_1 = 4.41 \pm 0.12$, $pK_2 = 6.26 \pm 0.15$, and $pK_3 = 13.9 \pm 0.1$ (Figure 1). pK_1 corresponds to the dissociation of the positively single charged reagent to give the neutral form and pK_2 and pK_3 correspond to the successive dissociations to give the single and double charged anions, respectively. The obtained values for these dissociations constants are similar to that of other thiosemicarbazones with oxime groups (*7, 8*).

Table I. Characteristics of DCDT Compounds

ion	pH	λ_{max}, nm	$10^{-3}\epsilon$, $L \cdot mol^{-1} \cdot cm^{-1}$
Fe(II)	<2	550	8.9
Fe(III)	5	410	8.4
Ni(II)	5	415	7.3
Ni(II)	9	385	7.9
Co(II)	<2	375	12.6
Mn(II)	9	375	6.4
Cu(II)	5	375	5.4
Cu(II)	9	365	5.1

Table II. Tolerance of Foreign Ions in the Determination of 3.0 $\mu g \cdot mL^{-1}$ Iron

min interfering foreign ion to Fe(II) ratio (w/w)	min interfering foreign ion to Fe(II) ratio (w/w)
<1	Co(II)
2	Te(IV)
5	Ni(II)
10	Mo(VI), Pd(II)
25	Ag(I), Cu(II), BO_2^-
50	Cr(III), Sn(II), Cr(VI)[a]
100	Al(III), Hg(II), Be(II), W(VI), F^-
>100	Zn(II), Cd(II), Pb(II), Bi(III), As(III), Mn(II), Ti(IV), Sb(III), Ca(II), Ba(II), Mg(II), V(V),[a] PO_4^{3-}, SO_4^{2-}, NO_3^-, Br^-, I^-, IO_3^-,[a] BrO_3^-,[a] ClO_3^-[a]

[a] In the presence of 1 mL of 10% ascorbic acid solution.

Table III. Determination of Iron in Wines

sample	iron found,[a] ppm	iron found by AA,[a] ppm
white wine 1	12.5	12.5
white wine 2	16.0	15.5
red wine 1	18.7	18.8
red wine 2	19.5	19.6
red wine 3	6.5	6.4

[a] Each value is the average of six separate determinations.

Table IV. Determination of Iron in Vegetables and Verdures

sample	iron found,[a] %	iron found by 2,2′-bipyridine method,[a] %
lentils	0.0205	0.0204
spinachs	0.0043	0.0043

[a] Each value is the average of six separate determinations.

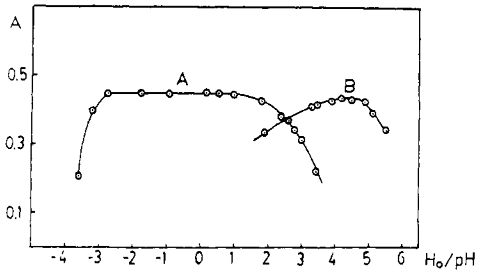

Figure 2. Influence of pH on formation of the complexes of DCDT with Fe(II) (A) and Fe(III) (B).

Oxidation-Reduction Behavior. The presence of reducing agents does not affect the reagent, whereas changes occur in the presence of oxidizing agents like H_2O_2. The reagent behaves like a reducing agent.

Qualitative Test. The reaction of DCDT with several inorganic ions at various pH values was tested. In Table I are the characteristics of the most important colored reactions.

Spectrophotometric Determination of Iron. The reagent DCDT reacts instantaneously in strongly acid medium with Fe(II) and Fe(III) ions to form a violet complex having λ_{max} at 550 nm. We have proved that the Fe(II) is the ion that forms the complex because this is obtained even in presence of ascorbic acid and the color does not appear in the presence of H_2O_2. In acetate buffer medium Fe(II) and Fe(III) ions form a yellow complex having λ_{max} at 410 nm. This complex must be of Fe(III) because the color does not appear in an inert atmosphere (by passing N_2) if the Fe(II) is used.

Effect of pH. The effect of pH on formation of Fe(II) and Fe(III) complexes was studied (Figure 2). A concentration 1.5 N of HCl was selected to prepare the samples for the iron determination. In these conditions the Fe(II) complex is formed.

Effect of Concentration of Reagent and Order of Addition. The color intensity remains constant with concentrations of the reagent above 10-fold molar excess; 1 mL of 1% reagent solution in a final volume of 25 mL was selected for the analytical procedure. The order of reagent addition was immaterial.

Stability. In the conditions of the recommended procedure, the complex of Fe(II) is stable at least for 6 h.

Composition of the Complex. The continuous variation and molar ratio methods were applied to the determination of the stoichiometry of both complexes of Fe(II) and Fe(III). Both methods show that the composition of the Fe(II) complex was 1:3 (iron to DCDT) and the composition of the Fe(III) complex was 1:2 (iron to DCDT). The overall conditional formation constant of Fe(II) complex by the González, Arrebola, and Román method (*9*) was found to be 1.43×10^{14}. According to literature data, the probable structure of the complexes would be as shown in Figure 3.

Calibration and Precision. The iron(II)-DCDT complex obeyed Beer's law in the range 0-6 $\mu g \cdot mL^{-1}$ iron. The molar

Table V. Determination of Iron in Minerals

standard sample	certified composition, %	iron certified, %	iron found,[a] %	error, %
magnesite-chrome, BCS No. 370[b]	SiO_2, 3.01; TiO_2, 0.13; Al_2O_3, 12.3; Cr_2O_3, 13.4; MnO, 0.11; CaO, 1.54; Na_2O, 0.06; K_2O, 0.03; Li_2O, 0.03	5.05	4.96	1.8
high-purity magnesite, BCS No. 389[b]	SiO_2, 0.89; TiO_2, 0.01; Al_2O_3, 0.23; Cr_2O_3, 0.28; Na_2O, 0.03; K_2O, 0.01; MnO, 0.008; B_2O_3, 0.029	0.199	0.20	0.5
Portland cement, BCS No. 372[b]	SiO_2, 21.3; TiO_2, 0.33; Al_2O_3, 5.35; CaO, 65.8; Mn_2O_3, 0.06; MgO, 1.3; Na_2O, 0.21; K_2O, 0.62; SO_3, 2.35; P_2O_5, 0.19	1.74	1.70	2.3

[a] Each value is the average of six separate determinations. [b] BCS: "British Chemical Standards" issued by Bureau of Analysed Samples, Ltd.

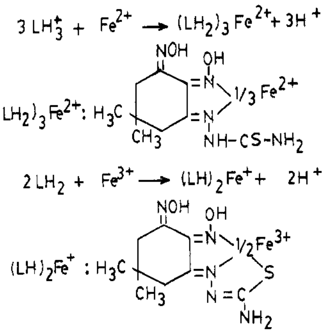

Figure 3. Probable structure of the Fe(II) and Fe(III) complexes with DCDT.

absorptivity was 8.9 × 10^3 L·mol^{-1}·cm^{-1}. The detection limit (*10*) was 0.05 μg·mL^{-1} of Fe(II) and the determination limit (*11*) was 0.1 μg·mL^{-1} of Fe(II). The optimum working range, as evaluated by Ringbom's method was 0.7–5.0 μg·mL^{-1} of iron. The relative error (11 determinations, 3.0 ppm of iron(II), 95% confidence level) is ±0.5%.

Effects of Foreign Ions. In the determination of 3.0 μg·mL^{-1} of iron, foreign ions can be tolerated (less than a 2.5% change in absorbance) at the levels given in Table II. The great selectivity of the method should be emphasized because only Co(II) interferes seriously.

Applications. In Tables III–V are the results obtained in the determination of iron in wines, foods, and minerals. These results are compared with those obtained by atomic absorption spectrophotometry or with 2,2′-bipyridine. These results are concordant and the proposed method is more rapid and easier.

Registry No. Fe, 7439-89-6; LH$_2$, 99688-02-5; (LH$_2$)$_3$Fe^{2+}, 99688-00-3; (LH)$_2$Fe$^+$, 99688-01-4.

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RECEIVED for review July 29, 1985. Accepted October 23, 1985.

Extraction–Spectrophotometric Determination of Tungsten as a Mixed Thiocyanate–Propericiazine Complex

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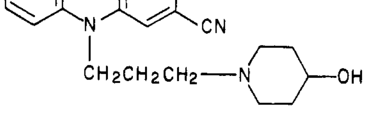
A new extractive spectrophotometric method for the determination of microgram amounts of tungsten, based on the extraction of yellow tungsten(V)–thiocyanate–propericiazine ion association complex into chloroform from 4.5–8.0 M hydrochloric acid medium is described. Beer's law is valid over the concentration range 0.6–14.8 ppm of tungsten. The complex, which is stable over a week, has an absorption maximum at 410 nm, and its molar absorptivity is 1.82 × 10^4 L mol^{-1} cm^{-1}. The effects of acid concentration, time, temperature, concentration of reagent, and the interferences from various ions are investigated. The proposed method is employed for the determination of tungsten in tungsten steel.

Several spectrophotometric methods have been reported for the determination of tungsten (*1–11*). Most of them are unsatisfactory for one reason or another. One of the most often used is the tungsten thiocyanate method (*1–8*) applied to either the aqueous solution or the organic extract. In these methods the interference of various metals, the stability of the complex, and the reproducibility have been the main problems. It was found during our investigation that the stability and the sensitivity of the tungsten–thiocyanate complex could be enhanced by adding 10-[3-(4-hydroxypiperidino)propyl]phenothiazine-2-carbonitrile ($C_{21}H_{23}ON_3S$) or propericiazine (PPC), which forms an ion association complex that can be extracted into an organic solvent. The structure of the PPC molecule is as follows:



The proposed method offers the advantages of rapidity, reproducibility, sensitivity, and selectivity without the need for heating the solution. The application of the method in the determination of tungsten content in tungsten steels has also been studied.

EXPERIMENTAL SECTION

Apparatus. A Beckman spectrophotometer (Model DB) with matched 1-cm silica cells was used for absorbance measurements.

Reagents. *Tungsten(VI) Solution.* A stock solution of tungsten(VI) was prepared from sodium tungstate (AnalaR) in double distilled water and standardized by the 8-hydroxyquinoline method (*12*). The stock solution was further diluted as required.

PPC Solution. A 2 × 10^{-2} M solution of PPC (Rhone Poulenc, Paris) in chloroform (AnalaR) was prepared and stored in an amber bottle and kept in a refrigerator for further use.

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