

**FLOTATION-SEPARATION AND SPECTROPHOTOMETRIC
DETERMINATION OF IRON(III) IN NATURAL WATERS,
STEEL SAMPLES AND PHARMACEUTICAL
FORMULATIONS USING 1-(3,4-DIHYDROXYBENZYLIDENE)
THIOSEMICARBAZIDE**

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ABSTRACT

A simple, sensitive and rapid flotation method has been proposed for the separation of Fe(III) using 1-(3,4-dihydroxybenzylidene)thiosemicarbazide (H₃BTS) as a chelating agent and oleic acid (HOL) as a collector. To optimize the flotation procedure, pH solution; concentrations of Fe(III), surfactant and H₃BTS; ionic strength; temperature and shaking time were studied. The influences of foreign ions on the recoveries and the determination of analyte ion were also examined. The Fe(III)-H₃BTS system was floated quantitatively (~100%) under the recommended conditions. The use of H₃BTS was successfully extended for the determination of Fe(III) spectrophotometrically at pH 7 and $\lambda = 566$ nm. The system obeys Beer's law over the concentration range of 0.077-8.490 mg.L⁻¹ with molar absorptivity of 0.16×10^4 L mol⁻¹ cm⁻¹. The detection limit (taken as three times the standard deviation of the reagent blank) is 0.069 mg L⁻¹ Fe(III) and the relative standard deviation (n = 10) was 2.7%. The proposed determination procedure was satisfactory applied to the analysis of Fe(III) in natural waters, vitamins and reference steel samples.

Keywords: Iron(III), 1-(3,4-dihydroxybenzylidene)thiosemicarbazide, Natural Waters, pharmaceutical formulations; steel samples; flotation; spectrophotometry.

1. INTRODUCTION

The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment [Igwa & Abia (2006)]. The rate at which effluents are discharged into the environment especially water bodies have been increased as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals. The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment [Igwa & Abia (2006)]. Iron is by far the most essential transition metal with a functional role in living systems. It occurs in conjunction with molybdenum in enzymes catalyze nitrogen fixation [Kabil & Ghazy (1995)]. It also plays an essential role in photosynthesis [Akl (2003)]. Moreover, iron ions are crucial for cell growth and it is generally accepted that tumor cells are more sensitive to iron deprivation than normal cells, which may to major extent be associated with cancer cells expressing higher levels of the iron-containing enzyme rib nucleotide reductase (RR) [Yemeli Tido et al., (2007)]. Accordingly, methodology for successive separation and/or determination of such ion is of great importance.

Numerous techniques for the preconcentration and/or separation of metal ions have been reported [Karimi et al., (2007); Leyden & Wegscheider (1981); Mizuike (1983) and Ghazy et al., (2006)]. These include evaporation of solvents, electrodeposition, liquid-liquid extraction, surface adsorption, precipitation, ion exchange, ion exchange impregnated materials, immobilized reagents, electro-osmosis and cloud point extraction. However, most of these methods suffer from inconveniences such as separation lengthy, limitation of the volume sample, time consuming, multistage, lower enrichment factor and consumption of harmful organic solvents. These problems can be overcome by using flotation techniques [Karimi et al., (2007); Leyden & Wegscheider (1981) and Ghazy et al., (2006)] which recently received a considerable interest owing to its simplicity, rapidity, economy, good separation efficiency (> 95 %) for small impurity agent concentrations ($10^{-6} - 10^{-2}$ mol L⁻¹) and a large possibility of applications for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose [Stoica et al., (1998)]. It is believed that this process incorporated as a clean technology to water

and wastewater treatment [Rubio et al., (2002)]. Therefore, the flotation technique was chosen for the separation process.

Ion flotation involves the removal of surface-inactive ions (colligend) from aqueous solution by adding surfactant which acts as collector. The subsequent passage of gas bubbles through the solution transfers the surface-active ions to the top [Doyle (2003) and Lazaridis et al., (2004)]. Compared to other separation methods, ion flotation has advantages in its ease of operation and low costs. It shows particular promise for treating large volumes of dilute aqueous solutions [Doyle & Liu (2003)].

Precipitate flotation [Rubin & Johnson (1967)] is a foam separation process used to remove surface inactive substances from aqueous dispersions. The component to be removed is precipitated before the addition of a surfactant (collector). This may be accomplished by adding any substance that forms an insoluble compound. Since the surfactant needs only to react with ions on the surface, small amounts of collector are required. Moreover, in this process the separation is obtained at the interface of the bulk and foam phases without the assistance from the extended phase, having the advantage of producing dry foam of small volume, and thus allowing the use of compact equipment [Rubin & Johnson (1967)].

Spectrophotometry still represents an alternative technique for the determination of metal ions in aqueous medium because of its simplicity, being inexpensive and is readily available [Ghazy and Mostafa (2002)]. Hence, spectrophotometry was selected for the determination of Fe(III) in this investigation. Although a vast number of reagents are available for the flotation-separation [Kabil & Ghazy (1995); Karimi et al., (2007); Rubin & Johnson (1967); Ghazy (1995); Hiraide et al., (1976); Takayanagi et al (1976); Sasaki et al., (1982) and Sasaki et al., (1982)] and/or spectrophotometric determination [Kabil & Ghazy (1995); Akl (2003); Ghazy (1995); Markzenko (1986); Hashmi et al., (1971); Hulanicki & Nieniewska (1974); Alexaki-Tzivanidou (1975); Pecar et al., (1975); Corigliano & Pasquale (1976); Poe et al., (1980); Lajunen & Aitta (1981); Salinas et al., (1987); Bayen & Das (1988); Abu-Baker et al., (1994); Malik & Rao (1997); Kara & Alkan (2001); Hashem et al., (2003); Zaijun et al., (2004); Tarafder & Thakur (2005) and Akl et al., (2006)] of Fe(III), no trial was made to float and analyze this analyte with H₃BTS. Therefore, the objective of the present work was to investigate the feasibility of developing the use of the

synthesized 1-(3,4-dihydroxybenzylidene)thiosemicarbazide (H₃BTS) chelating agent for the flotation-separation and spectrophotometric determination of Fe(III) in natural waters, vitamin and reference steel samples, under the recommended conditions.

2-EXPERIMENTAL

2.1. Apparatus

For the flotation process, the flotation cell (a cylindrical tube with a 15 mm inner diameter and 290 mm length, a stopcock at the bottom and a stopper at the top) was the same type as previously described [Ghazy et al., (2006)]. All spectral measurements were performed using a Unicam UV-2100 spectrophotometer. Measurements of pH were made using Hanna Instruments 8519 pH meter provided with a glass electrode. The Infrared spectra were recorded on Mattson 5000 FTIR spectrophotometer using KBr disc method. The concentration of iron in mother liquor, after flotation, was determined using a Pakin-Elmer atomic absorption spectrophotometer at 248.3 nm with an air-acetylene flame.

2.2. Reagents

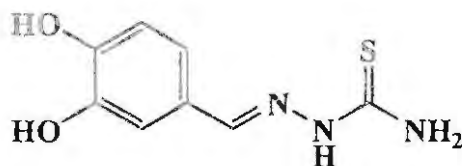
All reagents and solvents were of Analytical grade and were used without further purification. Bidistilled water was used throughout this study for washing and dilutions. All glassware was cleaned by soaking overnight in chromic mixture followed by washing with water. Oleic acid (HOL) was used directly as received. Its stock solution $6.36 \times 10^{-2} \text{ mol.L}^{-1}$ was prepared from food grade with specific gravity 0.895 (J. T. Baker Chemical Co.) by dispersing 20 ml in 1L kerosene. 3,4-Dihydroxybenzaldehyde (Aldrich grade) and thiosemicarbazide (Panreac grade) were used throughout. Fe(III) stock solution $1 \times 10^{-2} \text{ mol.L}^{-1}$ was prepared by dissolving the requisite amount of ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1:1 (v/v) Ethanol/water and standardized complexometrically with EDTA [Vogel (1973)]. HCl and/or NaOH were used for adjustment the pH. Thiel-Coch buffer solutions (pH 1.5-11.0) were prepared as previously reported [Britton & Robinson (1942)] by mixing 100 ml in different proportions of the following mixtures:

- a) 0.05 mol.L^{-1} oxalic acid + 0.20 mol.L^{-1} boric acid;
- b) 0.20 mol.L^{-1} boric acid + 0.05 mol.L^{-1} succinic acid + 0.05 mol.L^{-1} sodium sulfate;

c) 0.05 mol.L^{-1} sodium tetraborate and d) 0.05 mol.L^{-1} sodium bicarbonate.

2.3. Preparation of H₃BTS

1-(3,4-dihydroxybenzylidene)thiosemicarbazide (H₃BTS, Structure 1) was synthesized by condensation of equimolar amounts of 3,4-dihydroxybenzaldehyde and thiosemicarbazide in ethanol solution in the presence of few drops of glacial acetic acid. The reaction mixture was boiled under reflux for 6 h, evaporated and after cooling a reddish-brown precipitate of H₃BTS were obtained. The precipitate was filtered off, washed with ethanol, recrystallized from absolute ethanol and finally dried in a vacuum desiccator over CaCl₂. The purity was checked by elemental analysis, IR spectra and TLC. Its melting point was found to be 245°C and the stock solution, $1 \times 10^{-2} \text{ mol.L}^{-1}$ was prepared in ethanol.



Structure 1

2.4. Procedures

2.4.1. Flotation-separation

Ten ml of a solution containing $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) and $1 \times 10^{-4} \text{ mol.L}^{-1}$ H₃BTS were introduced into a flotation cell (fortunately, the resulting solution pH was in the range ~ 4.5 to 5.5, which is suitable for obtaining maximum flotation, ~100%). The cell was shaken well for 5 min to ensure complete complexation and 2 ml of $1 \times 10^{-3} \text{ mol L}^{-1}$ HOL were added. The flotation cell was then gently inverted upside down many times by hand, and then shaken for few seconds. Meanwhile, the stopper of the cell was removed to permit air movement. After 5 min standing for complete flotation, the concentration of iron in the mother liquor was determined by atomic absorption spectrophotometer at 248.3 nm. The flotability (F%) of the analyte was calculated by:

$$F\% = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f denote the initial and final concentrations of Fe(III) in the mother liquor, respectively.

2.4.1.1. Temperature

To study the effect of temperature on the flotation efficiency, a solution containing Fe(III) and H₃BTS and another containing the surfactant were either heated or cooled to the same temperature. The surfactant solution was quickly poured into the solution of the investigated ion (inside a cell jacketed with 1 cm thick fiberglass insulation) at time zero. The mixture was then floated according to the previous procedure under the optimum conditions.

2.4.2. Spectral measurements

A suitable aliquot containing known amount of Fe(III), specified for each investigation, was transferred to a 10 ml calibrated flask followed by 3 ml of Thiel-Coch buffer (pH ~ 7) and a suitable amount of H₃BTS. Then the volume was completed to 10 ml with bidistilled water. The solution allowed standing for 5 min and the absorbance was measured at 566 nm using the requisite amount of ligand and buffer as a blank.

2.5. Application

2.5.1. Natural water samples

The water samples were obtained from the Mediterranean sea (Ras El-bar and Gemsa cities), tap, Nile, underground (Mansoura city) and lake (Manzala Lake), Egypt. Each of pre-filtered water samples was poured into a beaker and 8 ml of concentrated HNO₃ and 3 ml of H₂O₂ (30 %) (for elimination and decomposition of the organic matter) were added. The sample, while stirring, was evaporated to one-tenth volume. After adjusting the sample pH to the desired value, the flotation and spectrophotometric determination were performed according to the recommended procedure.

2.5.2. Steel sample

The steel sample, kindly provided by Administration of Chemistry, Egypt, had the following composition 86.9 % Fe (by weight); C(0.0829%), S(0.0015%), P(0.0109%), Mn(0.324%), Ni (0.0792%), Cr (12.6%) and Mo (0.005%). A 391.135 mg sample was digested with 10 ml aqua regia and heated to near dryness, then mixed with 10 ml of concentrated nitric acid and heated for 30 min. The solution was then filtered, diluted and completed to 250 ml with 1:1 (v/v)

EtOH/H₂O. After adjusting the pH to 7, Fe(III) was determined spectrophotometrically.

2.5.3. Theregran Hematinic sample

Each Theregran M tablet (Bristol-Myers Squibb Company, Egypt) contains vitamin A (5000 IU), vitamin B1 (3 mg), vitamin B2 (3.4 mg), vitamin B6 (3mg), vitamin B12 (9 mcg), vitamin C (90 mg), vitamin D(400 IU), vitamin E(30 IU), niacin (20 mg), folic acid (400 mcg), pantathenic acid (10 mg), biotin (30 mcg), iron (27 mg), copper (2 mg), iodine (150 mcg), zinc (15 mg), magnesium (100 mg), calcium (40 mg), phosphorous (31 mg), chromium (15 mcg), molybdenum (15 mcg), selenium (10 mcg), manganese (5 mcg), chlorides (7.5 mg) and potassium (7.5 mg). As previously described [Ghazy et al., (2006)], one tablet was crushed; digested using 5 ml concentrated HNO₃ and heated to near dryness. After cooling, the residue was dissolved in another 5 ml of concentrated HNO₃ and the solution was gently evaporated. The residue was again heated with 50 ml distilled water, filtered off and diluted to 100 by absolute EtOH after adjusting the solution pH to ~7. A defined volume treated by the recommended procedure for the determination of Fe(III).

2.5.4. Haemoton sample

Each Haemoton capsule (GlaxoSmithKline Company, S.A.E. El-Salam City, Cairo, Egypt) supplies: ferrous fumarate (350.5 mg), vitamin B12(7.5 mcg), folic acid (2.0 mg), ascorbic acid (150.0 mg), manganese sulfate equivalent to (2.5 mg Mn) and copper sulfate equivalent to (2.5 mg Cu). The capsule was dissolved in 5 ml HNO₃ (1 mol.L⁻¹) and shaking well for 30 min, filtered off and diluted to 100 by absolute EtOH after adjusting the pH to ~7. The recommended procedure was used for determination of its Fe(III).

3- RESULTS AND DISCUSSION

3.1. Flotation-Separation process

In order to obtain the optimum conditions for maximum flotation of Fe(III), different factors affecting the process have been studied.

3.1.1. Effect of pH

According to our knowledge of flotation, the pH medium is highly significant that affects the metal-ligand system, firstly, it will be optimized [Ghazy & Mostafa (2008)]. Flotation experiments (using $1 \times 10^{-4} \text{ mol.L}^{-1}$ H_3BTS and $1 \times 10^{-3} \text{ mol.L}^{-1}$ of HOL surfactant) were carried out to establish the optimum pH for the flotation of $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) . The results are graphically illustrated in Fig.1. As can be seen, the flotability increases gradually as the pH increases, reaching maximum ($\sim 100\%$) at 4.5-5.5 then decreases. At pH 4.5-5.5, $\text{Fe(III)-H}_3\text{BTS}$ being made hydrophobic by combination with un-dissociated oleic acid, that begins to dissociate at $\text{pH} \geq 5.2$ [Ghazy et al., (2008)], through hydrogen bonding and/or chemically with oleate anions. These hydrophobic aggregates are floated to solution surface with the aid of air bubbles. Above pH 7, the flotability diminishes due to the solubility of the $\text{Fe(III)-H}_3\text{BTS}$ precipitate or the surfactant may give a white turbidity of sodium oleate dispersed in the whole bulk of the floating medium. Hence, a pH value of about 5 was selected for further flotation experiments.

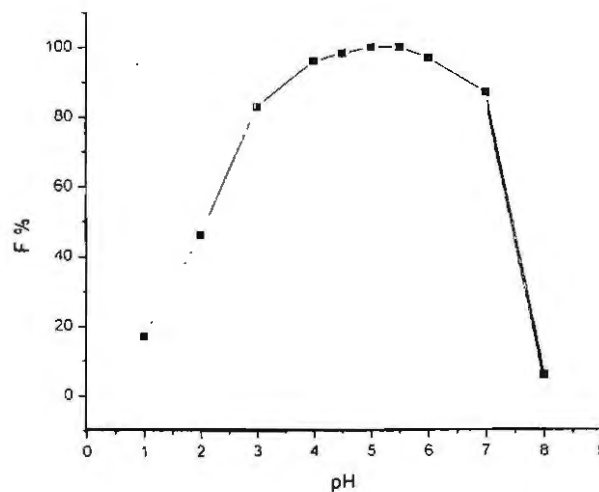


Fig (1): Flotability of $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) versus pH using $1 \times 10^{-4} \text{ mol.L}^{-1}$ H_3BTS and $1 \times 10^{-3} \text{ mol.L}^{-1}$ HOL.

3.1.2. Surfactant concentration

Trials were carried out to float Fe(III) with HOL only, but the recovery did not exceed 70% (Fig. 2A). Therefore, another series of

experiments were conducted to find the most suitable concentration of HOL surfactant for removing $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) ions from aqueous solutions of pH ~ 5 using $1 \times 10^{-4} \text{ mol.L}^{-1}$ H₃BTS (Fig. 2B). The flotability of Fe(III) was maximum when HOL concentration range is 1×10^{-3} - $5 \times 10^{-3} \text{ mol.L}^{-1}$, below which the flotation decreases due to the presence of insufficient amount of surfactant required for complete flotation. At higher surfactant concentration the decrease in the separation may be attributed to the surfactant changes the state of precipitates [Ghazy & El-Morsy (2008)]. The poor flotation at high surfactant concentration is caused by the formation of a stable, hydrated envelope of surfactant or, a hydrate micelle coating on the solid surface [Ghazy & El-Morsy (2008)]. As a result, the hydrophobicity of this surface was not satisfactory for flotation [Rubin & Johnson (1967)]. The surfactant concentration ($1 \times 10^{-3} \text{ mol.L}^{-1}$) was used.

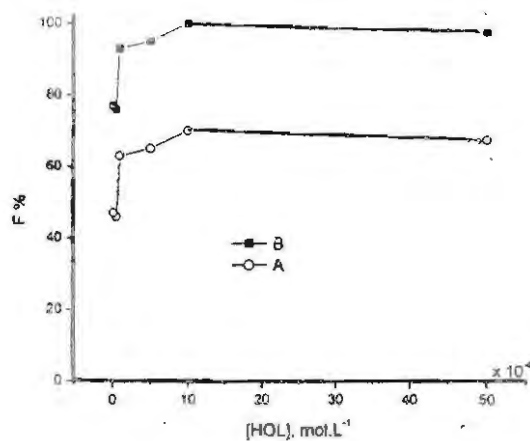


Fig (2): Flotability of $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) versus [HOL] at pH ~ 5 in the absence (A) and presence (B) of $1 \times 10^{-4} \text{ mol.L}^{-1}$ H₃BTS

3.1.3. Ligand concentration

The collecting ability of H₃BTS towards Fe(III) was examined to show the effect of different concentrations of H₃BTS on the flotability of the analyte using HOL at pH ~ 5 . The data showed that, the flotability of Fe(III) increases abruptly reaching its maximum percentage ($\sim 100\%$) at M:L ratio of (1:1). Excess collector has no effect facilitating the separation of Fe(III) from unknown matrices; $1 \times 10^{-4} \text{ mol.L}^{-1}$ H₃BTS was used.

3.1.4. Fe(III) concentration

Attempts to float different concentrations of Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5 were carried out. The results obtained (Fig. 3) show that the maximum flotation efficiency (~100%) of Fe(III) remain constant whenever the ratio of Fe(III) to H₃BTS is 1:1, 1:2. etc. The flotation begins to decrease at higher concentrations of Fe(III) attributed to the amount of H₃BTS is insufficient to bind all Fe(III) ions existing in solution.

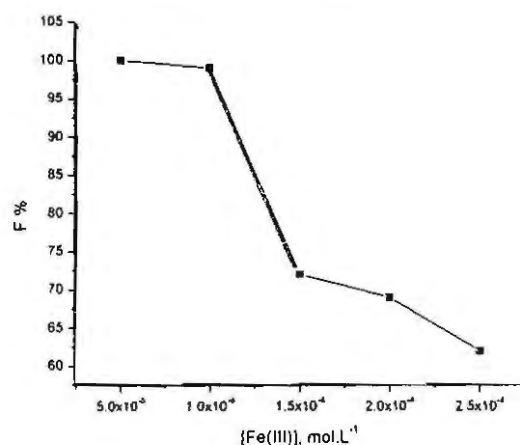


Fig (3): Flotability of different concentrations of Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5.

3.1.5. Temperature

The effect of temperature on the flotability of 5×10^{-5} mol.L⁻¹ Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5 was studied over a wide temperature range 5-90°C. The obtained data showed that the variation of temperature in this range has no marked effect on the flotation efficiency of Fe(III). Accordingly, all experiments (unless otherwise stated) were carried out at room temperature ($25 \pm 2^\circ\text{C}$).

3.1.6. Shaking time

The influence of shaking time on floating 5×10^{-5} mol.L⁻¹ Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5 was investigated. The data showed that a maximum flotation (~100%) was

attained after 3 min of shaking meaning that, the flotation-separation procedure is not time consuming.

3.1.7. Ionic strength

Table (1) summarizes the effect of varying the ionic strength of different salts on the flotation efficiency of 5×10^{-5} mol.L⁻¹ Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5. The salts used are generally similar to those present in natural water samples. It is clear that the ionic strength of the medium has not markedly affected the flotation process.

Table (1): Effect of ionic strength on the flotability of 5×10^{-5} mol.L⁻¹ Fe(III) using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5.

Salt	Concentration, mol.L ⁻¹	F (%)
KCl	0.01	100.0
	0.05	99.8
	0.10	99.5
NaCl	0.01	100.0
	0.05	100.0
	0.10	99.9
KNO ₃	0.01	100.0
	0.05	99.7
	0.10	99.7
CaCl ₂	0.01	100.0
	0.05	99.7
	0.10	99.5
MgSO ₄	0.01	100.0
	0.05	100.0
	0.10	99.7

3.1.8. Foreign ions

In order to assess the applicability of the proposed method to recover Fe(III) add to water samples, the effect of some foreign ions selected on the basis that they are normally present in fresh and saline waters was investigated. The tolerable amounts of each ion (presented as ion:Fe ratio) giving a maximum error $\pm 2\%$ in the flotation efficiency are summarized in Table 2. Close inspection of the data shows that the

cations and anions investigated did not interfere during flotation of Fe(III). However, some ions (ca. Zn^{2+} , CO_3^{2-} and $H_2PO_4^-$) can interfere at higher concentrations. This interference could be removed by increasing the concentration of H_3BTS .

Table (2): Effect of some foreign ions on the flotation of $5 \times 10^{-5} \text{ mol.L}^{-1}$ Fe(III) using $1 \times 10^{-4} \text{ mol.L}^{-1}$ H_3BTS and $1 \times 10^{-3} \text{ mol.L}^{-1}$ HOL at pH ~ 5 .

Cation	Foreign/Fe(III)	F (%)	Anion	Foreign/Fe(III)	F (%)
Na^+	10000	100.0	Cl^-	6900	100.0
K^+	10000	100.0	SO_4^{2-}	8000	100.0
Ca^{2+}	8000	100.0	NO_3^-	8000	99.7
Mg^{2+}	8000	100.0	ClO_4^-	1900	100.0
Mn^{2+}	5000	99.7	CO_3^{2-}	2.4	98.5
Co^{2+}	770	99.1	$H_2PO_4^-$	4	98.0
Ni^{2+}	2100	99.5	CH_3COO^-	1200	99.2
Cu^{2+}	3700	98.5			
Zn^{2+}	4	99.2			
Cd^{2+}	8000	99.9			
Hg^{2+}	9000	100.0			
Al^{3+}	800	100.0			

3.1.9. Application

In order to evaluate the capability of the flotation method for the recovery of Fe(III) from water, various types of water samples were selected in a way to provide a wide variety of sample matrices characterized by different types of interferents. The samples were pretreated as described previously. To 10 ml aliquots of investigated water sample, 3 or 6 mg.L^{-1} Fe(III) was added after adjusting pH of the medium to ~ 5 . The data obtained are presented in Table 3 and it is clear that they are satisfactory.

Table (3): Recovery (Re %) of Fe(III) ions added to 10 ml of some water samples using 1×10^{-4} mol.L⁻¹ H₃BTS and 1×10^{-3} mol.L⁻¹ HOL at pH ~5.

Type of Water (location)	Fe(III) added (mg.L ⁻¹)	Fe(III) found (mg.L ⁻¹)	Re %
Tap water (Our lab.)	3.00	3.00	100.0
	6.00	5.97	99.5
Nile water (Mansoura City)	3.00	3.00	100.0
	6.00	6.00	100.0
Sea water (Ras El-Bar)	3.00	3.00	100.0
	6.00	5.95	99.2
Underground water (Mansoura city)	3.00	3.00	100.0
	6.00	5.99	99.8
Lake water (El-Manzala lake)	3.00	3.00	100.0
	6.00	6.00	100.0

3.2. Spectral analysis of Fe(III)

3.2.1. Absorption spectra

Figure 4 shows the absorption spectra of Fe(III), H₃BTS and Fe(III)-H₃BTS. It was observed that Fe(III)-H₃BTS has an absorption band (566 nm) away from those of Fe(III) and H₃BTS. Accordingly, subsequent analysis of the colored complex was carried out at 566 nm.

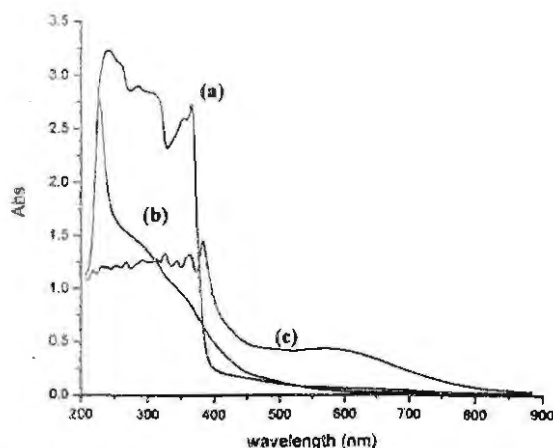


Fig (4): Absorption spectra of : (a) H₃BTS, (b) Fe(III) and (c) Fe(III)-H₃BTS

3.2.2. Effect of pH and medium

Various media like H₂O, EtOH, and Thiel-Coch buffer were introduced to examine their effects on the Fe(III)-H₃BTS systems. The results indicated that the color of the formed complex in Thiel- Coch buffer was stable for 24 h and has high sensitivity compared to the other media. Figure 5 shows that the absorbance of Fe(III)-H₃BTS system at 566 nm increases rapidly with increasing the pH of the solution up to pH 6.2 and remaining constant at 6.2-7.6 then decrease. Although, aqueous solution of Fe(NO₃)₃ is precipitated at pH > 3 [Kara & Alkan (2001)], the precipitate is readily dissolved on adding H₃BTS. Thus, pH ~7 was selected throughout the analysis of Fe(III) in this study.

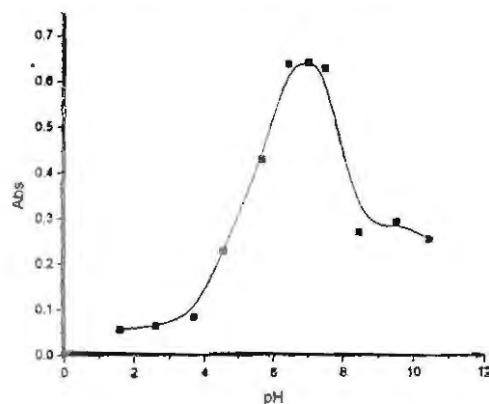


Fig (5): The effect of pH on the absorbance of Fe(III)-H₃BTS at 566 nm.

3.2.3. Composition of Fe(III)-H₃BTS

To study the stoichiometry of the complex, the spectrophotometric measurements were performed by the continuous variation method [Ghazy et al., (2006)]. The graph in Fig. 6 showed that a 2Fe : H₃BTS ratio is formed at pH ~7.

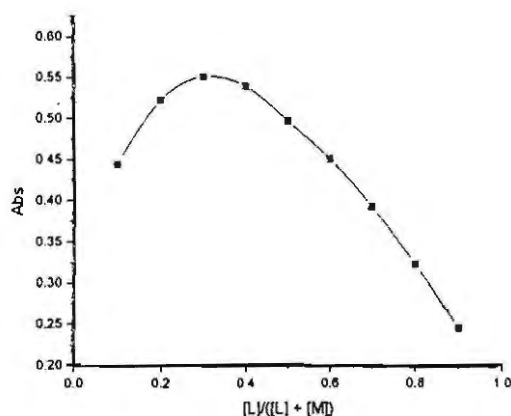


Fig (6): The determination of stoichiometry of Fe(III)-H₃BTS by spectrophotometric procedure at 566 nm and pH ~7.

3.2.4. Beer's law and sensitivity

Under the optimum conditions described in the recommended procedure, the applicability of H₃BTS as a spectrophotometric reagent for Fe(III) determination was studied at 0.062-10.04 mg.L⁻¹ of Fe(III) at pH 7 using 2×10⁻³ mol.L⁻¹ H₃BTS. The calibration graph in Fig. 7 is a straight line passing through the origin and obeys Beer's law over the concentration range 0.077 - 8.49 mg.L⁻¹ Fe(III) with a correlation coefficient (R) = 0.9997. The effective molar absorptivity (ε) at λ_{max} 566 nm was 0.16×10⁴ L. mol⁻¹.cm⁻¹ with a detection limit of 0.069 mg.L⁻¹ Fe(III), taken as three times the standard deviation of the reagent blank and a relative standard deviation of 2.7% for n = 10.

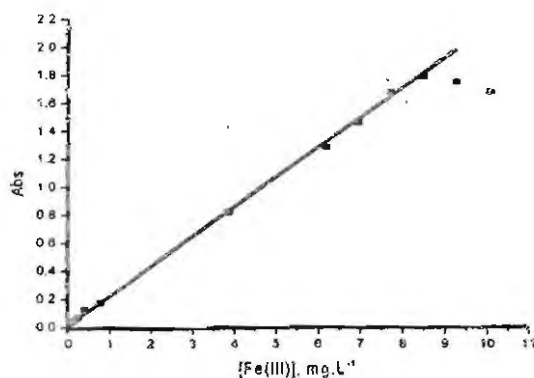


Fig (7): Calibration curve for the determination of Fe(III) at pH~7 using 2×10^{-3} mol.L⁻¹ H₃BTS.

3.2.5. Effect of foreign ions

To assess the usefulness of the proposed method, the effect of the investigated diverse ions on Fe(III) analysis was studied (Table 4). The interfering cations were added as chlorides while the anions as sodium salts. The tolerance of the method with respect to foreign ions was investigated with solutions containing 5.59 mg.L^{-1} Fe(III) and various amounts of foreign ions. The tolerance criterion for a given ion was taken as the deviation of the absorbance by more than ~2% from the value expected for the system Fe(III)-H₃BTS. Inspection of the data shows that most of the investigated ions at high ion: analyte ratio did not interfere. However, Al(III), Ba(II), Cu(II), citrate and bicarbonate ions interfere when added with more than 2 folds of Fe(III). The interferences could be overcome by adding excess H₃BTS. EDTA interfered seriously which may be attributed to a competition between EDTA and H₃BTS for chelation with Fe(III).

Table (4): Effect of foreign ions individually on the determination of 5.59 mg.L⁻¹ of Fe(III).

Foreign ion/Fe(III)	Ion
800	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , NH ₄ ⁺ , Cl ⁻ , NO ₃ ⁻ , HCOO ⁻ , CH ₃ COO ⁻ , O ₄ ²⁻
500	Mn ²⁺ , SCN ⁻
200	Zn ²⁺ , Ni ²⁺
60	Co ²⁺ , CO ₃ ²⁻
10	Cd ²⁺
2	Al ³⁺ , Cu ²⁺ , Ba ²⁺ , ClO ₄ ⁻ , HCO ₃ ⁻ , citrate
1	EDTA

3.2.6. Analytical applications

The spectrophotometric procedure was applied for the determination of Fe(III) spiked to different water samples including tap, Nile, lake and Underground waters (Table 5).

Also, the procedure was applied for the analysis of Fe(III) in two certified vitamin tablets and a reference steel sample (Table 6). As seen, the recovery of Fe(III) is satisfactory and sensitive with RSD% not exceed 2.28%. Moreover, the data were confirmed by atomic absorption spectrometry (AAS) which indicate the capability of the proposed procedure in the determination of Fe(III) in natural water samples, vitamins and steels.

Table (5): Determination of Fe(III) spiked to natural water samples by spectrophotometric method.

Water	Fe(III) added (mg.L ⁻¹)	Spectrophotometry			AAS		
		Found (mg.L ⁻¹)	R (%)	RSD (%)	Found (mg.L ⁻¹)	R (%)	RSD (%)
Distilled water	0.5	0.492	98.2	1.6	0.497	99.4	0.60
	1.5	1.496	99.7	0.27	1.500	100.0	0.00
Tap water	0.5	0.499	99.8	0.20	0.500	100.0	0.00
	1.5	1.498	99.9	0.73	1.495	99.6	1.00
Nile water	0.5	0.495	99.0	1.00	0.500	100.0	0.00
	1.5	1.500	100.0	0.00	1.499	99.9	0.20
Lake water	0.5	0.499	99.8	0.20	0.500	100.0	0.00
	1.5	1.497	99.8	0.60	1.495	99.7	1.00
Underground water	0.5	0.493	98.6	1.40	0.498	99.6	0.73
	1.5	1.500	100.0	0.00	1.500	100.0	0.00

Table (6): Analysis of Fe(III) in vitamin tablets and reference steel sample.

Sample	Certificate (mg l ⁻¹)	Spectrophotometric procedure		AAS procedure	
		Found (mg l ⁻¹)	RSD (%)	Found (mg l ⁻¹)	RSD (%)
Reference steel sample	1359.60	1347.00	0.93	1350.00	0.71
Theragran-M vitamin	27.00	26.77	0.84	26.80	0.74
Haemoton	350.00	345.00	1.43	342.00	2.28

CONCLUSION

1-(3,4-Dihydroxybenzylidene)thiosemicarbazide reacts rapidly with Fe(III) ions to give a violet precipitate (at relatively high concentration) and soluble olive-green (at relatively low concentration). The proposed flotation procedure is optimized for separation of 5×10^{-5} mol L⁻¹ Fe(III) in presence of 1×10^{-4} and 1×10^{-3} H₃BTS and surfactant, respectively, at pH 5 with efficiency ~ 100% at 25 °C. The analyte was determined below 10 µg.L⁻¹ using H₃BTS at 566 nm with $\epsilon = 0.16 \times 10^4$ L.mol⁻¹.cm⁻¹ and the method is successfully applied to natural water, vitamin tablets and a reference steel sample by spectrophotometric method without interferences. The proposed method is sensitive and improved the detection limit (0.069 mg L⁻¹) with RSD of 2.28%.

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الفصل التعويمي و التقدير الطيفي لأيونات الحديد الثلاثي في عينات من المياه الطبيعية والصلب وعينات دوائية باستخدام ١-(٣،٤-ثنائي هيدروكسي بنزليدين) ثيوسيميكر بازيد

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تهدف الدراسة لإيجاد طريقة سهلة وبسيطة وسريعة وانتقائية لفصل أيونات الحديد الثلاثي بتقنية التعويم عن طريق استخدام ١-(٣،٤-ثنائي هيدروكسي بنزليدين) ثيوسيميكر بازيد كعامل ترابط وحمض الأوليك كعامل سطحي نشط . تم أيضا دراسة الظروف المثلى لعملية الفصل التعويمي مثل تأثير الأس الهيدروجيني للمحلول وتركيز كل من عامل الترابط ، العامل السطحي النشط وأيونات الحديد كذلك تم دراسة عامل القوة الأيونية للمحلول ودرجة الحرارة وتأثير وقت الرج على اتمام هذه الخطوات بكفاءة قد تصل الى ١٠٠%. تم أيضا فصل أيونات الدراسة بنجاح من عينات بعض المياه الطبيعية. امتدت الدراسة لاستخدام ١-(٣،٤-ثنائي هيدروكسي بنزليدين) ثيوسيميكر بازيد بنجاح في تقدير أيونات الحديد الثلاثية باستخدام القياس الطيفي عند الرقم الهيدروجيني ٧ وطول موجي ٥٦٦ نانوميتر وتم تطبيق قانون بيرز-لامبرت والذي يطاع في مدى من التركيز من ٠.٠٧٧ ، الى ٠.٨٤٩٠ ميلليجرام/ لتر و امتصاصية مولارية $10^4 \times 0.16$ لتر/مول. سنتيمتر وتم تطبيق الطريقة بشكل مرضي في تحليل أيونات الحديد المضافة الى عينات من المياه الطبيعية والفيتامين وعينة قياسية من الحديد الصلب.

