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ARTICLES

Synthesis, Spectral Studies and Complexation Properties of *N*,*N*'-bis(5-bromo-salicylidene)-2-hydroxy-1,3-propanediamine (BSHP) and Iron Extraction with BSHP from Oils[1]

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Abstract—A Schiff base was synthesized by reaction of 1,3-diamino-2-propanol and 5-bromo-2-hydroxy benzaldehyde. The Schiff base *N*,*N*'-bis(5-bromo-salicylidene)-2-hydroxy-1,3-propanediamine (**BSHP**) was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, UV-Vis spectral studies. The complexation of iron with BSHP was investigated spectrophotometrically. The extraction of iron from oil phase to aqueous phase was carried out with BSHP. Extraction conditions were optimized using central composite design. Optimum extraction conditions were found to be 32°C, 2 mL/g for the ratio of the volume of the Schiff base solution to the amount of oil, and 11 min for the stirring time. The method has been validated by using oil based metal standard, obtaining satisfactory results. The limit of detection (**LOD**) of the improved method is 0.04 μg/g. It has been applied to analysis of different oil samples. The concentrations of iron in olive, sunflower and corn oils were found to be 0.65 ± 0.02, 0.41 ± 0.01, 0.36 ± 0.03 μg/g, respectively. A simple, cheap, rapid, efficient, sensitive and accurate alternative analytical method for the iron determination in oils has been presented in this paper.

Keywords: Schiff base, iron, extraction, oil, atomic absorption spectroscopy

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There are various studies in the chemistry of the metal complexes of Schiff bases due to wide application of their complexes in different fields [1–8]. It is known that ligands containing different donor atoms such as O and N type form stable complexes with metals [9]. Therefore, chemists are extending their investigations to new Schiff bases containing O,N ligand system which forms stable complexes with metal ions. Many investigations are related to the structure, bonding, antimicrobial and antifungal activities, complex properties and stability of Schiff base-metal complexes but few have been directly concerned with analytical applications [10].

Iron is an important nutrient in the human diet as it is complexed with hemoglobin and plays a major role in respiratory enzymes such as cytochromes [10]. However, effects of iron on the oxidative stability of edible oils are reported in the literature [11–13]. Iron is a potential contaminant of oil deriving from the processing equipment [11]. Different detection techniques such as FAAS [12], ICP-OES [11], GFAAS [12,14], ICP-MS [13, 15, 16] were used for the determination of iron in oils. However, some techniques of sample treatment such as wet, dry or microwave digestion are required to eliminate the organic matrix of oils. Acid digestion has some disadvantages such as risk of explosion or contamination as well as long time required, etc. In our previous work, a new method for the determination of iron in oils which does not require a digestion step was improved [17].

In the present article, a Schiff base has been synthesized, characterized and utilized as an analytical reagent for the extraction and spectroscopic determination of iron. The Schiff base is characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, UV-Vis spectral studies. Furthermore, the Schiff base has been used as a complexing agent for the extraction of iron from various oil samples into aqueous phase. In this study, the optimization of experimental conditions (temperature, the ratio of Schiff base/oil and stirring time) for the iron extraction has been succeeded by applying central composite design optimization method and the determination of iron in oils by flame atomic absorption spectrometry (**FAAS**) has been achieved properly after the extraction.

[1] The article is published in the original.

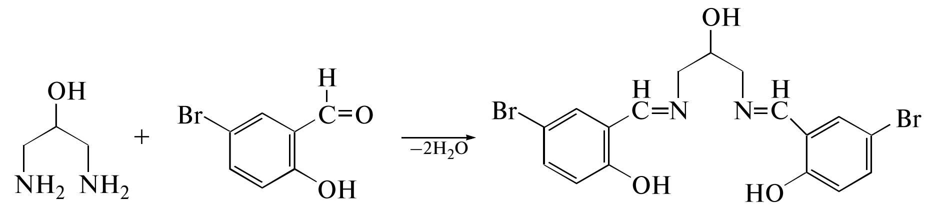

Fig. 1. Synthesis scheme for the preparation of the ligand (BSHP).

EXPERIMENTAL

Chemicals and instrumentation. A Merck Titrisol 109972 iron stock solution (1000 μg/mL iron; $FeCl_3$ in 15% HCl) was used for preparing the aqueous standard solutions for calibration in FAAS measurements. Conostan iron standard in oil (5000 μg/g; code no. 508619) was used as oil based metal standard for optimization of experimental extraction conditions and testing the improved method. *N*,*N*'-bis(5-bromo-salicylidene)-2-hydroxy-1,3-propanediamine (BSHP) was synthesized and the structure of this Schiff base was clarified. BSHP solutions were prepared by dissolving appropriate amounts of ligand in 70% (v/v) ethanol–water mixture and kept in polyethylene containers that protect them from the light and heat. All the reagents were analytical grade, and water purified by reverse osmosis system was used throughout.

The electronic spectra of the Schiff base and the complex in UV-Vis region were recorded in 70% (v/v) ethanol–water using PG Instruments Ltd T80 UV-Vis spectrometer. The IR spectra were recorded with a Perkin-Elmer BX+1600 model FT-IR instrument in KBr pellets. The elemental analysis was conducted on Leco CHNS 932 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avence DPX-400 spectrometer. A Perkin Elmer AAnalyst 200 atomic absorption spectrometer was used for the determination of iron in aqueous solution. A Thermo Orion 5 Star model pH meter and Heidolph MR 3001 K model magnetic stirrer were also used. Perkin Elmer Optima 3100 XL ICP-OES and Mars 5 Microwave Digestion System were used for comparison study.

Synthesis of ligand (BSHP). BSHP was prepared through the condensation reaction of 1,3-diamino-2-propanol and 5-bromo-2-hydroxy benzaldehyde in alcoholic media. Figure 1 demonstrates the preparation of BSHP. A solution of 1,3-diamino-2-propanol (10.00 mmol) in 40 mL of absolute ethanol was added to a solution of 5-bromo-2-hydroxy benzaldehyde (20 mmol) dissolved in 40 mL of absolute ethanol at 40°C. The yellow precipitate was filtered off, washed with ethanol and subsequently dried in open air. Anal. calc. for $C_{17}H_{16}Br_2N_2O_3$ (mol wt 456.13): C, 44.76; H, 3.54; N, 6.14. Found: C, 45.14; H, 2.84; N, 6.20%.

Complexation properties of BSHP. Electronic absorption spectra of BSHP and Fe–BSHP were recorded in 70% ethanol–water (v/v) solvent mixture at 25°C. The absorption spectra of the solutions of 1.5×10^{-5} M for the ligand and complex are given in Fig. 2. Because the spectra of the ligand and complex are overlapped on a large scale, the difference between the measured absorbance and the calculated theoretical absorbance of the excess ligand is considered as corrected absorbance (A_{corr}) value.

The effect of pH change on the absorbance of complex was studied with a UV-Vis spectrophotometer. The ratio of the buffer solution to the final solution volume was 1 : 10 for each investigated mixture for the adjustment of pH. In order to specify completeness of complex formation reaction, kinetic studies were carried out.

Optimization of experimental conditions. To designate the optimum conditions in the procedure of extracting iron from oil phase to aqueous phase, central composite design has been applied [18, 19]. The temperature, the ratio of the volume of BSHP (1.0×10^{-3} M) to oil mass (V_{BSHP}/m_{oil}, mL/g) and the stirring time were chosen as the factors that influence the extraction efficiency of iron. The factors, the levels and their values are given in Table 1.

In the extent of the central composite design optimization procedure, 20 experiments should be done [17–19]. Accordingly, 20 experiments shown in

Table 1. Levels and the values of levels used in central composite design

		Levels				
		−1.682	−1	0	+1	+1.682
x_1 (1st factor)	Temperature, °C	16.59	20	25	30	33.41
x_2 (2nd factor)	V_{BSHP}/m_{oil} ratio, mL/g	0.318	1	2	3	3.682
x_3 (3rd factor)	Stirring time, min	1.59	5	10	15	18.41

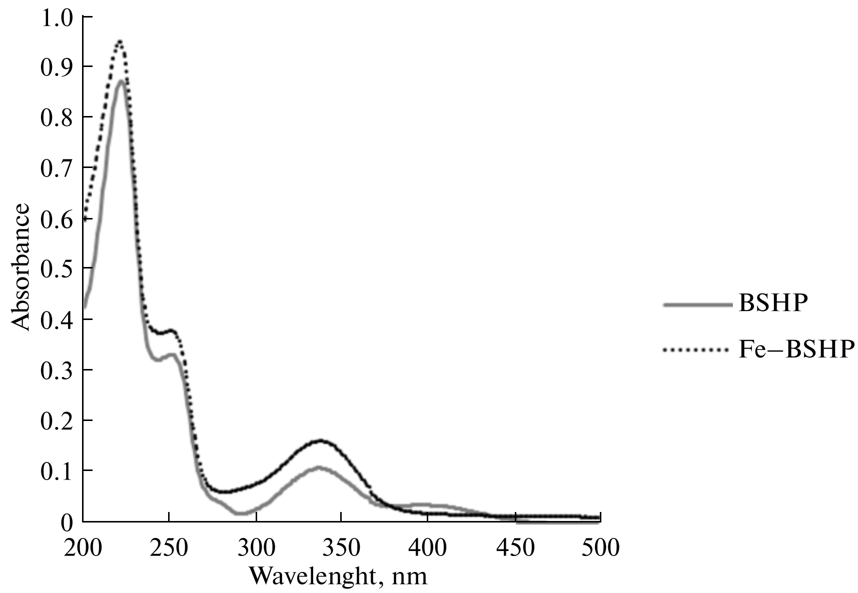

Fig. 2. The electronic absorption spectra of 1.5×10^{-5} M BSHP and its Fe(III) complex in 70% ethanol–water.

Table 2 were carried out as part of the optimization procedure. The iron concentrations in standard sample solutions prepared by appropriate dilution of oil based metal standards were fixed to be 10 μg/g. The iron concentrations of the extracts gained from each experiment were determined by FAAS. Corresponding equations were constructed by means of iron concentrations and solved using software according to the

Table 2. Experiments in the extent of the central composite design

Experiment	x_1 Temperature, °C	x_2 V_{BSHP}/m_{oil}, mL/g	x_3 Time, min	Recovery, %
1	20	1	5	71.80
2	30	1	5	91.80
3	20	3	5	90.98
4	30	3	5	90.98
5	20	1	15	95.08
6	30	1	15	89.34
7	20	3	15	93.44
8	30	3	15	94.67
9	25	2	10	96.72
10	16.59	2	10	94.67
11	33.41	2	10	98.77
12	25	0.318	10	69.60
13	25	3.682	10	92.05
14	25	2	1.59	94.26
15	25	2	18.41	97.95
16	25	2	10	101.23
17	25	2	10	90.98
18	25	2	10	90.57
19	25	2	10	92.62
20	25	2	10	95.49

central composite design method as in the literature [17–19].

Application of the method. The developed method was applied to some oil samples under the optimum extraction conditions. The oil sample was mixed with 1×10^{-3} M Schiff base solution at optimum V_{BSHP}/m_{oil} ratio and stirred under the optimum conditions given in Table 3. The ethanol-water phase (extract) including iron complex was separated, decomposition of the complex was succeeded by adding conc. HNO_3 (5 mL of extract : 1.25 mL of acid) and then iron concentration was determined by FAAS. Iron determination in oils by ICP-OES after microwave digestion with HNO_3 was also used as the proof of the improved method.

RESULTS AND DISCUSSION

Spectral characterization of ligand. The IR spectra were recorded in the range 400–4000 cm^{-1}. The IR spectrum of BSHP exhibits band at 1636 cm^{-1} corresponding to the stretching vibration of the C=N Schiff base group [20–22]. In general, the absorption bands appearing at around 1635 cm^{-1} are assigned to the stretching vibration of C=N group [22, 23]. The ^{1}H NMR spectrum of the ligand (BSHP) displayed the presence of the signal at δ 8.44 ppm due to the Schiff base imino group. Furthermore, the ^{13}C NMR spectrum of BSHP exhibited the signal belongs to imine carbon at δ 167.2 ppm.

Spectra and composition of complex. Figure 2 shows the absorption spectra for BSHP and Fe–BSHP at pH 4 in wavelength range 200–500 nm. The composition of complexes was determined by mole ratio and continuous variation methods. Graphs given in Figs. 3 and 4 confirmed a 1 : 1 (M : L) composition for Fe–BSHP. Spectrophotometric data were used to calculate the formation constant of 1 : 1 Fe–BSHP complex by applying multicomponent analysis method [24]. The formation constant was found to be $(1.7 \pm 0.2) \times 10^7$.

Table 3. Optimum extraction conditions for Fe(III) by BSHP

Temperature, °C, x_1	V_{BSHP}/m_{oil} ratio, mL/g, x_2	Stirring time, min, x_3
32	2	11

Effect of pH. The complex formation reactions of metal ion with BSHP depend on pH. In order to find the optimum pH, the effect of pH in the range 4–8 on the complex formation reactions of Fe with BSHP was investigated. Due to the fact that the structure of the ligand could degrade, the effects of pH on the complexation were not investigated at pH < 4. Moreover, considering the possibility of saponification of oil and the precipitation of metal hydroxides, the effects of pH on the complexation were not studied at pH > 8. From the results, it was observed that the complex exhibits maximum absorbance at pH 4 (Fig. 5). Thus, further studies were carried out at pH 4 of acetate buffer solution.

Time effect. The absorbance values of Fe–BSHP complex were monitored at 10 sec intervals during 60 min in order to measure completeness of complex formation. The complex formation was completed in approximately 1 min. Therefore, absorption measurements were performed at 1 min after mixing of reagents.

Optimum experimental conditions for iron extraction from oils. The extraction conditions for iron should be optimized in order to get the most effective results. For the optimization, 20 experiments were achieved, as mentioned in Table 2. The results obtained from these experiments were transformed into the corresponding equations and solved using software according to the central composite design method.

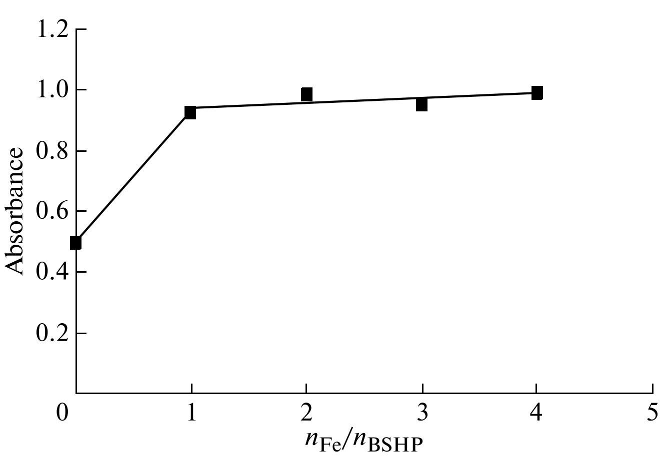

Fig. 3. Mole ratio method for Fe–BSHP at λ = 336 nm, pH 4.

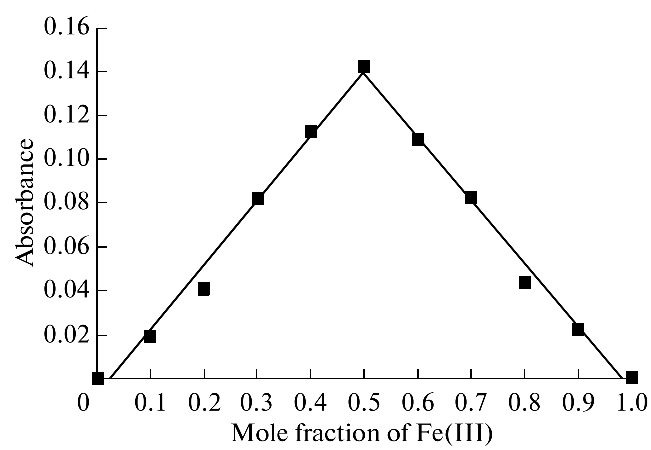

Fig. 4. Continuous variation method for Fe–BSHP at λ = 336 nm, pH 4.

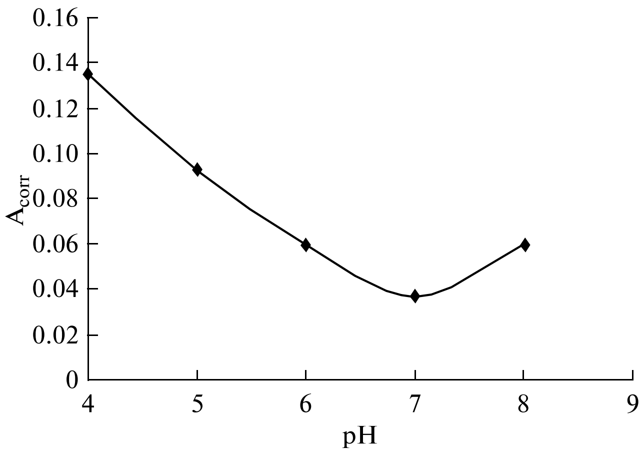

Fig. 5. The effect of pH on A_{corr} signal of Fe–BSHP.

Hence, the optimum values of the factors: the temperature, the ratio of the volume of used Schiff base solution to the amount of oil (V_{BSHP}/m_{oil}, mL/g) and the stirring time were calculated and presented in Table 3.

Applications. The improved extraction procedure was applied to the oil based metal standard under the optimum conditions. The certified value of iron was 10.00 μg/g and obtained value was 9.81 ± 0.08 ($n = 5$). The t-test (for a 95% confidence interval) was performed in order to check if there was any significant difference between the certified and obtained values; no significant difference was observed. The LOD of the method is 0.04 μg/g, which was calculated as the concentration equivalent to the three times the standard deviation (3σ) of the signal of the blank oil standard solution. LOD for Fe is lower than the one established in refined vegetable oils, 1.5 μg/g [13, 25]. To demonstrate the applicability of the improved extraction method to real samples, it was applied to the determination of iron in olive, sunflower and corn oils, which contain iron in different amounts. Concentration of iron in the oil samples was determined by FAAS. For comparison, the same oil samples were also analyzed by ICP-OES after microwave digestion as reported before [26]. The results obtained from each method are given in Table 4. According to the student's t-test, t values were calculated as 2.37, 1.18 and 0.86 for olive, sunflower and corn oils, respectively. At the 95% confidence level, critical t value is 2.78. As can be seen, all t values are lower than critical value; this confirms that no significant difference between the proposed and conventional methods.

Table 4. Determination of iron in commercial oil samples by proposed and conventional methods ($n = 3$)

Sample	Iron concentration, μg/g	
	Proposed method[a]	Conventional method[b]
Olive oil	0.65 ± 0.02	0.68 ± 0.003
Sunflower oil	0.41 ± 0.01	0.44 ± 0.04
Corn oil	0.36 ± 0.03	0.34 ± 0.02

Note: [a]—FAAS determination after extraction with BSHP.
[b]—ICP-OES determination after microwave digestion.

* * *

The present paper reports on the synthesis, characterization and complexation properties of a Schiff base and iron extraction from oils with this ligand. The improved extraction procedure provides a sensitive and simple approach for the determination of iron in oil samples by FAAS. The method is simple, rapid and does not require any drastic, time consuming or risky pretreatment, such as concentrated acid leaching.

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