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Preconcentration of Iron in Some Drug and Water Samples by Coprecipitation with Magnesium Hydroxide Before Spectrophotometric Determination

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Abstract: A method was purposed for preconcentration and determination of iron, in this study. The method consist of these steps respectively: I) Coprecipitation of the iron present in the sample with $Mg(OH)_2$ collector. II) Seperation of the precipitate by centrifuging. III) Solving the precipitation in acid. IV) UV-VIS spectrophotometric determination of the iron concentrated in the resultant lower volume solution using its complexation with thiocyanate. The effects of factors such as centrifugation time, pH and Mg concentration on the absorbance signal were investigated and the optimum values of these factors were determined. Total iron in the sample was brought single oxidation state (Fe(II) or Fe(III)) before coprecipitation procedure. Calibration curve was derived for both of the proceses. The detection limit and working range for the proposed method were found to be 0.01 mgL^{-1} and 0.03-0.3 mgL^{-1} respectively. The proposed method was applied to tap water, mineral water samples and Rennie anti-acid drug tablet. The accuracy of the method was tested by analyte spiked method. The accuracy results in terms of Recovery % are between 90-100%. Mostly the relative standart deviations (RSD %) values do not exceed 5%.

***Keywords*:** Iron determination, preconcentration, coprecipitation, $Mg(OH)_2$ collector, UV-VIS absorpsiyon spectrophotometric method.

Bazı ilaç ve Su Örneklerinde Demirin Spektrofotometrik Tayin Öncesi Mağnezyum Hidroksit ile Birlikte Çöktürme Yoluyla Önderiştirilmesi

Özet: Bu çalışmada demir için bir önderiştirme ve tayin yöntemi önerilmektedir. Yöntem sırasıyla şu adımlardan ibarettir: I) $Mg(OH)_2$ kollektörüyle örnekteki demirin birlikte çökmesi II) Oluşan çökeleğin santrifüjlenerek ayrılması, III) Çökeleğin asitte çözülmesi IV) Elde edilen daha düşük hacimli çözeltide deriştirilmiş olan demirin tiyosiyanatla kompleksleşme yoluyla UV-VIS spektrofotometrik olarak tayin edilmesi. Santrifüjleme süresi, pH, Mg derişimi gibi etkenlerin çökmeye veya absorbans sinyaline etkileri araştırılmış ve bu etkenlerin optimum değerleri belirlenmiştir. Örnekteki toplam demir, birlikteçöktürme öncesi tek bir yükseltgenme haline (Fe(II) or Fe(III)) dönüştürülmüştür. Prosesin her ikisi için kalibrasyon grafiği oluşturulmuştur. Yönteme ait 0.01mgL^{-1} tespit sınırı ve 0.03-0.3 mgL^{-1} çalışma aralığı elde edilmiştir. Yöntem musluk suyuna, maden suyu örneklerine ve Rennie antiasit ilaç tabletine uygulanmıştır. Yöntemin doğruluğu analit aşılama yoluyla test edilmiştir. Elde edilen doğruluk değerlerinin çoğu yüzde geri kazanım olarak % 90-100 arasındadır. Tekrarlanabilirlik veya kesinlik için ise bağıl standart sapma olarak çoğunluğu % 5'i geçmeyen değerler elde edilmiştir.

***Anahtar Kelimeler*:** Demir tayini, demir önderiştirilmesi, birlikte çöktürme, $Mg(OH)_2$ kollektörü, UV-VIS Spektrofotometrik metod.

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1. INTRODUCTION

The biological significance of the trace elements is widely investigated. Trace element determinations are of continuous importance due to their biological importance as well as the quality control of products manufactured in the industry, especially those of high purity.

Heavy metals are known as toxic. However, lower levels of some heavy metals are essential for human organism. One of them is iron. After entering to the organism, iron follows a complex path. Besides carrying oxygen by bonding it to hemoglobin, it exists in the structures of some vital enzymes.

The coprecipitation methods are a branch of the field of methods of seperation and enrichment. Such methods are usually based on adsorption, to be retained by a precipitate called as collector.

More than thirty types of collectors were used in this field studies. Those used before 1982 were compiled by Minczewski et al in tables to indicate the preconcentrated species and applied examples related to each one [1]. Most of ones used later are given in Table 10 (in this article); the studies shown in this table were chosen to include those related to the iron preconcentration after 1997. $Mg(OH)_2$ is one of the collectors used in this field. The studies on the use of this collector for the iron preconcentration are consisted of the seperation of iron from metallic lead sample and its determination by o-phenanthroline extraction spectrophotometric method [2], the preconcentration of iron in ocean water and its determination by ICP-MS (See Table 10, references 6, 16, 22)

A review of the literature has revealed that there is no study that used the simple UV-VIS spectrophotometric method among the iron determination methods after proconcentration. It also has been found that there is no study which uses drug sample in preconcentration methods by coprecipitation. It should be noted that preconcentration and determination of a trace type that is unmentioned in drug prospectuses is of particular importance. The study in this article involves the preconcentration of iron by coprecipitation. In the present study, an alternative method for the preconcentration and determination of iron has been purposed. This alternative method employs iron as analyte, $Mg(OH)_2$ as collector, and a simple UV-VIS spectrophotometric as a method of analysis. As a simple UV-VIS spectrophotometric method, well-known thiocyanate complexation method was chosen. By doing so, it is aimed to bring the advantages of coprecipitation and UV-VIS spectrophotometric methods together so that they will complement each other. It is believed that this method will be useful for such demands of the institutions with shoestring budgets that conduct routine analysis. Furthermore, the proconcentration and determination of iron was handled in Rennie anti-acid tablet for the first time. The Fe impurity detected by the proconcentration in this drug tablet is a beneficial impurity thanks to the biological importance of iron.

2. EXPERIMANTAL

2.1. Apparatus

UV-VIS Spectrophotometer: UNICAM UV / VIS Spectrometer UV 2

Centrifuge: Hettich Rotofix, 32A and Hettich Universal 320

PH meter: Adwa AD8000

2.2 Reagents and solutions

All solutions were prepared from analytical grade Merck liquid and solid agents. Double distilled water was used as solvent water. 1) Fe(II) and Fe (III) Standards: a) Stock solutions, which each was 1000 mgL^{-1} concentration, were prepared from iron salt, weighted solid was dissolved in 0,01 M HCI. b) 10 ppm Fe(II) and Fe(III) standards were prepared from these stock solutions. The mediums of these diluted solutions were created with about 0.01 M HCI (iron hydroxide precipitation was seen in even 10 mgL^{-1} concentration when not being acidificated), 2) Solid Na_2SO_3 and as an alternative 2 % (w/V) Na_2SO_3, 3) 1 M $MgSO_47H_2O$ 100 mL, 4) 6 M NaOH 1000 mL, 5) 2 M HCI 1000 mL, 6) 2 M HNO_3 500 mL, 7) Saturated $K_2S_2O_8$ (K-peroxodisulfate) solution: Some grams were transferred to a small beaker by taking from the solid compound, it was mixed for a while after adding water, then it was waited. Upper clear solution was used. (This solution should not be more 3 days when it is used), 8)1.83 M KSCN, 100 mL.

2.3 Proposed method; preparing calibration curve and applying to the samples

A series of 50 mL Falcon centrifuge tubes are obtained to use some of them for calibration curve and some others for samples. 10 mgL^{-1} Fe (the standard is chosen for Fe(II) or Fe(III) depending on for which one the calibration curve will be prepared) is added to the tubes at the rate of between 150-1500 µL so as to achieve 0.03-0.3 mgL^{-1} Fe when diluted to 50 mL. Following this, double distilled water is added to the tubes up to thick marks pointing 50 mL. These 50 mL samples are added to the tubes chosen for samples. 1 M $MgSO_4$ is added to the tubes for calibration curve according to Table 4. It should be noted that $MgSO_4$ is not added to the sample if the Mg concentration in the analysed sample is known; if not known, 200 µL is added. Thereafter, the pH of each solution is set to 12. After waiting for 15-20 minutes, it is centrifuged at 4000 rpm for 20 minutes. Following that, the supernatant solution is removeded. 4.0 mL of 2M HCl is added to each tube. When all the precipitate dissolves, 100 µL saturated $K_2S_2O_8$ solution and 900 µL 1,83 M KSCN are added and mixed. Absorbance values are taken from the UV-VIS spectrophotometer at 470 nm.

2.4 Sample preparation

Sample preparation is performed in two means/roads: 1) *Reduction:* The total iron, which is assumed to be a mixture of Fe (II) and Fe (III) ions in the sample, is converted into Fe (II) and coprecipitated. 2) *Oxidation:* The total iron is converted into Fe (III) and coprecipitated as Fe (III). The calibration curve is prepared according to Fe (II) in the first and Fe (III) in the second.

2.4.1 Tap water sample preparation

1) Reduction road: I) About 1 L of tap water is added to a large beaker. II) It is filtered. III) Solid Na_2SO_3 (0.1-0.2) g is added to the filtrate and it is mixed for an hour. As an alternative to solid reductant, it is Na_2SO_3 solution. Instead of adding only one time to orginal sample, 100 µL %2 Na_2SO_3 can be added to each tube after adding sample to tubes one by one.

2) Oxidation road: The step I and II described above are applied exactly. III) 2.5 mL of concentrated HNO_3 and a tip of spatula (0.1 - 0.2 g) of solid potassium peroxydisulfate ($K_2S_2O_8$) are added to 1 L of filtered sample to. IV) It is left to heat and mixed; it is mixed at least for an hour without exceeding 40 ℃ V) It is cooled to the room temperature.

Table 1. The sample compositions.

Samples species	Composition
Model sample A	$As\ mgL^{-1}$ Fe(II): 0.12, Fe(III): 0.08, Mg(II): 96, SO_4^{2-} : 0.21, NO_3^- : 0.26, Cl^-: 7.10
Model sample B	$As\ mgL^{-1}$ Fe(II): 0.2, Cu(II): 0.1, Co(II): 1, Mg(II): 96, Mn(II): 1, Cr(VI):1.2, Cr(III):1, Ni(II):1.4, Hg(II): 0.4, Cd(II):1.2, Ca(II):8, Na^+:32.2 K^+:63.5, HCO_3^- : 61, SO_4^{2-}: 76.8, Ac^-:0.2, NO_3^- : 6.7, Cl^-:14.2
C. Ü tap water	Unknown (no in formation available)
Beypazarı mineral water	$As\ mgL^{-1}$ Ca(II):235.5, Mg^{2+}:108.4, Al^{3+} : 0.0087, Na^+:265.2, K^+:63.01, NH_4^+: 0.05, HCO_3^- :1865.4, SO_4^{2-} :138, Cl^- : 25.8, F^- : 0.46, $NO_3^- < 1.0$, $NO_2^- < 0.005$, Silikat: 62.5, Fosfat:1.9 (given on bottle)
Eskipınar mineral water	$As\ mgL^{-1}$ Ca(II): 235.5, Mg^{2+}:108.4, Na^+: 265.2, K^+: 0, NH_4^+:yok-, HCO_3^- :2501, SO_4^{2-}:26.4, Cl^- : 30.7, F^- : 0.14, no NO_3^-, no NO_2^- , no silicate, no phophate (given on bottle)
Rennie antiacid tablet	Active ingredients: 680 mg calcium carbonate, 80 mg magnesium carbonate; inactive ingredients: sugar, potato starch, pregelatinized corn starch, magneisum stearate, talcum, liquid paraffin, light mint flavor, lemon flovar (given in drug propectus).

2.4.2 Mineral water sample preparation

Table 2. Relations of sample type, Mg concentration, sample preparation method and calibration curve

Sample species	Mg concentration in sample, mgL^{-1}	Sample preparation method	St. of analyte for calibration curve	Adding volume of 1M $MgSO_4$, for calibration curve, µL
Model Sample A	96 (0.004 M)	reduction	Fe(II)	200
Model sample B	96	b	Fe(II)	200
C.Ü. tap water	not known	reduction	Fe(II)	180[c]
	not known	oxidation	Fe(II)	180[c]
Beypazarı mineral water	108.4 (4.5×10^{-3} M)	reduction	Fe(II)	225
	108.4 (4.5×10^{-3} M)	oxidation	Fe(III)	225
Eskipazar mineral water	126 (5.2×10^{-3} M)	oxidation	Fe(III)	260
Rennie antiacid tablet	91.4[a] (3.8×10^{-3} M)	oxidation	Fe(III)	190

a This value was achieved by solubilizing 4 tablets in 1 L
b No reductant or oxidant are added
c This value is obtained by experimentally

1) Reduction road: I) About 1 L of mineral water is taken into a beaker. II) It is wait for a period for the outgassing to complete. 6 M NaOH is added dropwise to get a pH 7 or slightly above providing no precipitation. III) A tip of spatula (0.1- 0.2 g) of solid Na_2SO_3 is added and it is mixed for an hour. If alternative reductant is added, it must be followed to above presedure

2) Oxidation road: 1) About 1 L of mineral water is taken into a large beaker. II) Once the outgassing is complete, add a tip spatula (0.1- 0.2 g) of solid potassium peroxydisulfate ($K_2S_2O_8$) and 2.5 mL of concentrated HNO_3. III) It is left to heat and mixed; it is mixed for an hour without exceeding 40 ℃. V) It is cooled to the room temperature.

2.4.3 Rennie antacid tablet sample preparation

Oxidation method is employed for this sample. I) 4 tablets (app. 5 g) are weighed on the analytical balance with an accuracy of ±0,0001 g. (More than 4 tables for 1 L causes excessive foaming and the filtering difficulty). II) It is transferred to the 1 L beaker. 200 mL double distilled water and 200 mL 1 M HNO_3 are added gradually. III) A tip of spatula (0.1- 0.2 g) solid potassium peroxydisulfate ($K_2S_2O_8$) is added once the outgassing and foaming are finished. IV) It is heated and mixed; it is mixed at least for an hour without exceeding 40 ℃ . V) It is cooled down to the room temperature and filtered. The volume is completed to 1 L by adding water

3. RESULTS AND DISCUSSIONS

3.1 Predicted parameters

Concentration factor was designed to be 10 (sample volume is 50 mL, final volume is 5 mL after separation). The final volume, which would be 5 mL, was designed to be as the sum of the following three volumes and agents: 1) 4.00 mL precipitate dissolvent acid, 2) 100 µL saturated $K_2S_2O_8$ (oxidant), 3) 900 µL KSCN (complexing agent). Pre-addition concentrations of these three reagents were calculated based on the volume parameters given for the spectrophotometric thiocyanate method considered in the literature [3] and appropriate concentrations of these three reagents in the measurement medium. These values are shown in Table 3. Absorpsion peak is observed at 470 nm.

Table 3. Volumes and concentrations of the regeants that will be added to the separated precipitate.

Added reagent	Concentration in the measurement medium given in the literature	Predicted volume	Calculated concentration
HCl	0.48 M	4.00(∓0,02) mL	2 M[b]
$K_2S_2O_8$	0.5 mL doy/50 mL[a] (as $(NH_4)_2S_2O_8$)	100 µL	100 µL doy/5 mL[c]
KSCN	0.33 M	900 µL	1.83 M

a 0.5 mL satured $(NH_4)_2S_2O_8$ added in 50 mL total volume.
b Calculated conc. 0.6 M, but 2M is taken considering that Mg $(OH)_2$ will be solved
c 100 µL saturated $K_2S_2O_8$ is added in 5 mL total volume

3.2 Effect of centrifugation time

In order to find out the proper centrifugation time, centrifugations for different times were performed. 3 repetitive measurement were conducted for each time (n=3). Other conditions and factors are kept as the same for each one. 4 repetitive measurements were carried out for each time, Centrifugation rate at 4000 rpm, Measurements were given in Table 4.

Table 4. Effect of centrifugation time on precipitation (50 mL of 0.2 ppm Fe, 1000 µL of 1 M $MgSO_4$ and 500 µL of 5 M NaOH were added to each tube, n=4).

Time, min	Absorbance	Increase in signal, %	RSD (%)
10	0.318	-	<5
20	0.339	11.7	<5
30	0.351	3.5	<5

As seen in Table 4, the signal increases in parallel to the increase in the time. However, this increase becomes insignificant after 20 minutes and lower than the RSD of the measurements. The increase in signal is 11.7% when the time increases from 10 minutes to 20 minutes. This increase is greater than the RSD % 5. When the duration increases from 20 minutes to 30 minutes, the increase in absorbance is 3.5% which is lower than the RSD of signals, 5%. Therefore, 20 minutes is found to be sufficient.

3.3 Effect of pH

To a solution containing 50 mL of 0.1 mgL^{-1} Fe(II) in a number of tubes, 200 µL of 1 M $MgSO_4$ was added. Various amounts of NaOH solutions were added at various concentrations to obtain media at different pHs. After waiting for 15-20 minutes, they were centrifuged for 20 minutes and then the pH of each was measured before the supernatant solution was discarded. After the solutions of which pH values were measured were discarded, each precipitate was dissolved in 4.00 mL 2 M HCl and 100 µL of saturated $K_2S_2O_8$ and 900 µL of KSCN were added. Absorbance readings were taken at 470 nm. Effect of pH on absorbance was shown in Figure 1.

According to graph in Figure 1, the signal is increasing up to pH 10.2 It remains constant between 10.2 and 12.3. It increases again after 12.3. The optimal pH range is 11-12. The optimal pH is assumed to be 12 rather than the middle of the optimal range (i.e. 11-12) for Mg to achieve a complete precipitate. At this pH value, $Ca(OH)_2$ precipitation cannot be observed.

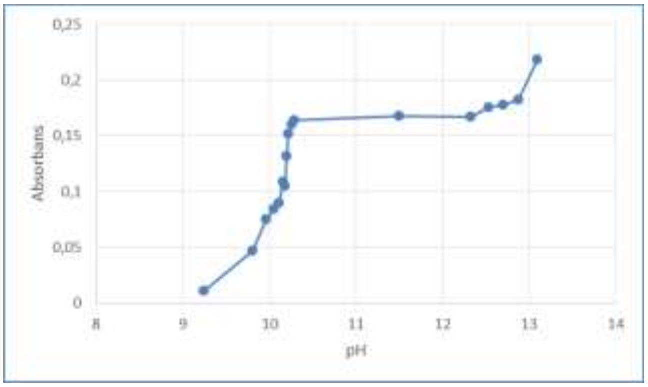

Figure 1. Effect of pH on absorbance (Medium: 0.1 mgL^{-1} Fe(II) st, 4×10^{-3} M Mg(II).

3.4 Effect of Mg^{2+} concentration

It was done also parallel adding of each adding. 500 µL of 10 ppm Fe^{2+} was added in each tube and the concentration of Fe(II) was set to 0.1 mgL^{-1} by completing the volumes to 50 mL adding water. Following this, 1000 µL of 1 M $MgSO_4$ was added to the reference and between 100-1000 µL of 1M $MgSO_4$ added to the others. Then, 700 µL of 6 M NaOH was added. Then, It was waited for 15-20 minutes and centrifuged for 20 minutes. After centrifugation and supernatant solution discarding the same operations as in Section 2.2 are applied. Plotting the absorbance against Mg reactivate volume has provided Figure 2.

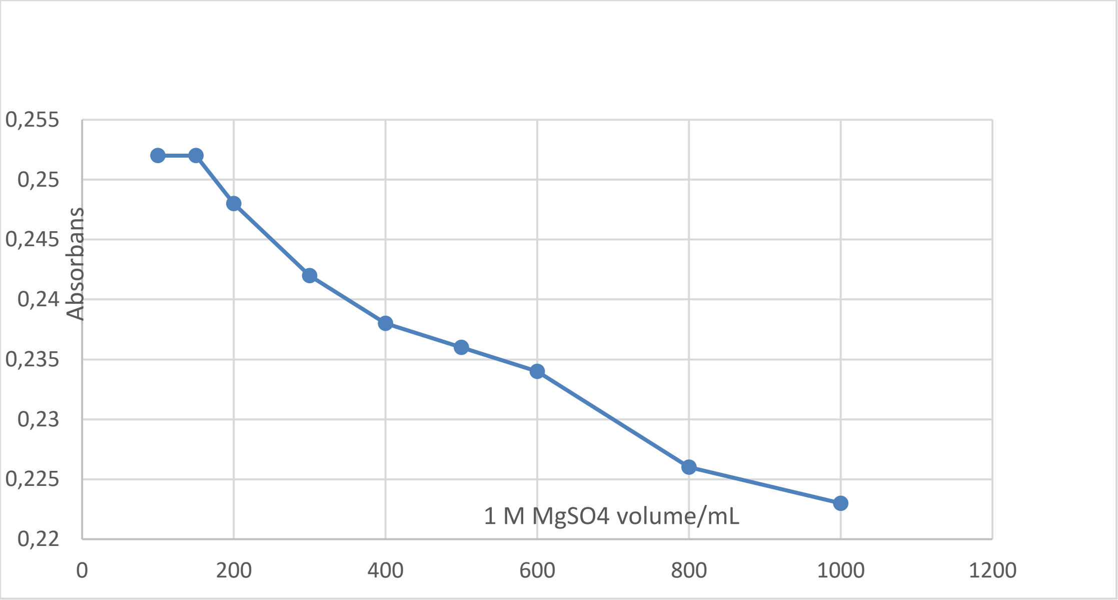

Figure 2. The effect of added 1M $MgSO_4$ volume. (Medium: 50 mL of 0.1 mgL^{-1} Fe(II) and 700 µL of 6 M NaOH solution were added to each tube.

According to the Figure 2, the signal reduces with increasing Mg concentration. However, this reduction is insignificant and the difference between the maximum and minimum absorbances is not more than 0.030 (close to the blank test signal). The optimal value was accepted to be 200 µL. However, this value is taken only to be added to the calibration curve standards that would be prepared for the analysis of water samples with the unknown Mg concentrations. If Mg is present in the sample and its concentration is specified on the label or prospectus, Mg of sample is used as a collector. For these kinds of samples, Mg reagent with equivalent concentration to that of in the sample is added to the standards of calibration curves. Whether its concentration is known or not, $MgSO_4$ is not added to a sample which contains Mg. Mg of samples is used as collector.

3 .5 Interferences

When investigating the interference of heavy metal ions, a grouping was made as: Amphoter ones and not amphoter ones. Any interferences cannot be expected for amphoter ones because they would be polyatomic and anionically ionized in the alkaline precipitation medium of the method. Only, investigation of Cr(VI) interference from this group was considered to be sufficient. For not amphoter ones, trace toxic metals that can be present in water, that are, Cd(II), Co(II), Cu(II), Cr(III), Hg(II), Mn(II), Ni(II) and, the interference of KF ve $NaHCO_3$ species were investigated. For this purpose, different volumes of solution standards of which interference to be studied were added to the tubes. Then 50 mL of 0.2 mgL^{-1} Fe(II) standard solution, 200 µL of 1 M $MgSO_4$ solution and 600 µL of 6 M NaOH solution was added to each tube. Then, the known procedures were applied. The results are given in Table 5. The tolerance limit (tolerable limit) was taken as the interfrent concentration or the corresponding interfrent / analyte ratio, which changed the absorbance by ∓5 %.

Table 5. Tolerance limits of some ions. Medium: 50 mL of 0.2 mgL^{-1} Fe(II), 200 µL of 1 M $MgSO_4$ and 600 µL of 6M NaOH solution were added to each tube. (n=3).

Species (Sp)	**[Sp] /[Fe] ppm/ppm**	**Tolerable limit, mgL^{-1}**	**Species (Sp)**	**[Sp] /[Fe] ppm/ppm**	**Tolerable limit, mgL^{-1}**
$CaCl_2$	11400	2280	Hg(II)	230	46
Cd(II)	>300	>60	Mn(II)	>1000	>200
Co(II)	15	3	Ni(II)	>200	>40
Cr(III)	20	4	KF	>750	>150
Cr(VI)	100	20	$NaHCO_3$	>2050	>410
Cu(II)	1.2	0.24			

Table 6. Parameters of the calibration curves for the proposed determination method (with concentration) and the determination method without concentration (for with preconcentration method to each tube: Fe st added was dilueted to 50 mL, Table 2 was followed for the values be added of 1 M $MgSO_4$. pH was set to 12, centrifugation rate 4000 rpm, centrifugation time 20 min., 4.00 mL 2 M HCl to each precipitate 100 µL of saturated $K_2S_2O_8$ and 900 µL 1,83 M KSCN were added. Absorbance read at 470 nm).

Parameter type	**The method without preconcentration**	**The method with preconcentration (The proposed method)**	
		According to Fe(II)	**According to Fe(III)**
Linear regression equation	A= 0.151c + 0.007 (c: mgL^{-1})	A = 1.802 c + 0.024	A=1.866c + 0.042
Corelation constant/ r^2	0.998	0.999	0.998
Measurement/peak wavelength /λ_{maks} (nm)	470	470	470
molar absorption coefficient (Lmol^{-1}cm^{-1})	8.4×10^3	1.0×10^5	1.1×10^5
Sandell`s sensitivity[a] (ng/cm^2)	6.6	0.63	0.57
Dedection limit 3s/m (mgL^{-1})	0.12	0.01	0.01
10s/m (mgL^{-1}) quantization limit	0.4	0.03	0.03
working interval (mgL^{-1})	0.4- 20	0.03-0.30	0.03-0.30
Concentration factor[b] (or preconc. factor)	-	10	10
Improvement factor[c]	-	11.9	12.3

a Concentration rise which causes to an increase of 0.001 in absorbance in a spectrophotometer with 1cm beam length [4]

b The ratio of sample volume preperated before separation to the sample volume after separation

c The ratio of the LR equation slope of the proposed method to the LR slope of the method without preconcentration

3.6. Calibration curve parameters

By applying the optimal values obtained above, the calibration curve and related parameters were obtained. Differently, Table 2 was followed for the volume value be added of 1 M $MgSO_4$. The parameters of the calibration curves for the with preconcentration method (proposed method) and without preconcentration method are shown in Table 6.

The slop of the linear regressions equations obtained through the proposed method is ten times more than that of the other method without preconcentration (see Table 6). Thus, the calibration sensitivity is increased at least ten times in the proposed method.

3.7 Applicability of the method

The accuracy of the presented method was tested on model the samples by direct comparison and on the real samples by analyte spiked methods. The sample compositions are given on Table 1. The comparison results on the model sample are given in Table 7. The findings obtained from the analyte spiked method on the real samples are presented in Table 8.

From Table 7, Table 8 and Table 9, it is obvious that most of the RSD values are in the acceptable range while only a few are above 5%. These RSD figures are sufficient to prove the precision of the proposed method. In terms of the validness, most recovery % values are above 90 % supporting the accurty of the proposed method.

Table 7. Application of the proposed methods on model samples (50 mL of sample was added to each tube. The $MgSO_4$ solution was not added to this sample or to any samples. The pH adjustment and subsequent operations are as in Table 6.

Sample	**Known Fe conc., mgL^{-1}**	**Found value, mgL^{-1} $\bar{x} \pm ts/\sqrt{n}$ ***	**Recovery (%)**	**Relative st. deviation (RSD%)**	**Sample preparation method/conversion**
Model sample A	0.20	0.203 ±0.010	101	1.9	Reduction (100 µL of 2% Na_2SO_3 was added to each tube)
Model sample B	0.20	0.206 ±0.003	103	1.7	No reductant or oxidant was added

* 95% confidence level, n=3, t=4.30 for model sample A; n=5, t=2.78 for model sample B, $\bar{x}$ **:** Mean values.

Table 8. Application of the proposed methods on water samples by conversion into Fe(II) and testing its accuracy by the analyte spiked method. After sample and iron standards additions, other operations that continue with pH adjustment are as in Table 6.

Sample	**Added conc., mgL^{-1}**	**Found value, mgL^{-1} $\bar{x} \pm ts/\sqrt{n}$ ***	**Rec. (%)**	**RSD (%)**	**Sample preperation method/ conversion**
C.U. tap water	0	0.030 ± 0.005	-	6.3	Reduction (by adding solid Na_2SO_3)
	0.04	0.070 ± 0.003	101	1.8	
	0.08	0.107 ± 0.010	96	0.4	
	0.12	0.146 ±0.008	96	2.2	
	0.16	0.183±0.006	96	1.4	
C.U. tap water	0	0.016 ±0.004	-	10	Reduction (by adding 100 µL 2% Na_2SO_3 to each tube)
	0.04	0.052 ±0.003	91	1.9	
	0.08	0.093 ± 0.004	97	2.0	
	0.12	0.132 ± 0.006	97	2.0	
Beypazari mineral water	0	0.006 ±0.004	-	25	Reduction (by adding 100 µL 2% Na_2SO_3 to each tube)
	0.04	0.041 ±0.002	94	1.5	
	0.08	0.075 ± 0.004	87	1.9	
	0.16	0.149 ±0.006	90	1.5	

* %95 confidence level, n=3, t= 4.30, $\bar{x}$ **:** Mean values

There is a relation between sample preparation method with accuracy for water samples. Higher accuracy was achieved by reduction for water samples. Oxydation method was preferred for antiacid tablet because sample preparation for antiacid tablet is necessarily initiated with acid addition. Further, the oxidation method which is compatible with this medium requires less work. In the reduction method, solid Na_2SO_3 and 2 % Na_2SO_3, which can substitute each other as a reductor, produced results with closed accuracy.

Table 9. Application of the proposed methods on water and antiacid tablet samples by conversion to Fe(III) and testing its accuracy by analyte spiked method. After sample and iron standards additions, other operations that continue with pH adjustment are as in Table 6.

Sample species	**Added conc., mgL^{-1}**	**Found volue, mgL^{-1}** $\bar{x} \pm ts/\sqrt{n}$ *	**Recovery (%)**	**RSD (%)**	**Sample preperation method / conv.**
C.U. tap water	0	0.010 ± 0.001	-	3.0	Oxidation (conversiyon to Fe(III) by adding solid $K_2S_2O_8$)
	0.04	0.045 ± 0.0002	87	0.2	
	0.08	0.077 ± 0.004	83	2.0	
	0.12	0.107 ± 0.002	80	1.0	
	0.16	0.134 ± 0.004	77	5.8	
Beypazari mineral water	0	0.012 ±0.016	-	53	
	0.04	0,048 ±0.004	89	3.4	
	0.08	0.083 ± 0.006	89	3.1	
	0.12	0.116 ± 0.005	87	1.6	
	0.16	0.159 ±0.011	92	2.8	
Eskipazar mineral water	0	0.011 ±0.001	-	5.2	
	0.04	0.046 ±0.014	88	12.2	
	0.08	0.078 ± 0.004	85	2.2	
	0.12	0.115 ±0.014	88	4.9	
	0.16	0.155 ±0.049	90	13	
Rennie antiacid tablet	0	0.241 ±0.084	-	1.6	
	0.04	0.296 ±0.014	136	2.0	
	0.08	0.312 ±0.057	89	7.3	
	0.12	0.338 ±0.013	81	1.6	
	0.16	0.379 ± 0.049	86	5.2	

* %95 confidence level, n=3, t= 4.30

3.8 Compare the same field with other methods

The detection limit of the proposed method is larger than that of most of the methods given in Table 10. There are two reasons for this; 1) Instrument 2) Preconcentration factor. The analytical instrument UV-VIS absorption spectrophotometer used in the proposed method is not used by any of the methods given in Table 10. As seen Table 10, there are 23 studies of which 15 used FAAS, 5 used ICP-AES and 4 used ICPMS. The detection limits of these istrument are lower than that of an UV-VIS spectrophotometer; that is, they are more sensitive.

Table 10. Studies into the preconcentration of iron by coprecipitation between 1997 and 2015 in literature

Analytes	**Collector**	**Fe detection limit, μgL^{-1}**	**CF**^{a}	**Instru-ment**	**Sample**	**Reference**
Cu, **Fe,** Pb, Mn, Zn, Cd, Ni, Bi, Cr	Co-DDTC	54	75-225	FAAS	Dialysis samples, sea water	[5]
Fe	$Mg(OH)_2$	0.003	14	ICPMS	Sea water	[6]
Se, Cu, Pb, Zn, **Fe** Co, Ni, Mn, Cr, Cd	Co-DDTC	4	40	ICP-AES	River and waste water samples	[7]
Fe(II), F**e(III),** Pb	$LaPO_4$	b	10	ICP-AES	Water samples	[8]
Al, Au, Bi, Cd, Co, Cu, **Fe**, Mo, Ni, Pb,Pd Ti, V, W, Zn	MnO_2	5	80	FAAS ICP-AES	Natural water samples	[9]
Cu(II), **Fe(II)**, Cd(II),Pb(II), Co(II), Ni(II)	Zn-HMDTC-HMA	36.1	25-500	FAAS	Waste water, certified cediment and zinko samples	[10]
Co, Cr, Pb, **Fe**	$Er(OH)_3$	0.67	25	FAAS	Soil, urine, sediment, and natural water samples	[11]
Fe(III), Pb, Bi	YPO_4	0.08	20	ICP-AES	Metal and Cl^- salt solutions of Co^{2+}, Ni^{2+} Cu^{2+}	[12]
Cr(III), **FeIII** Pb(II), Mn(II)	$Eu(OH)_3$	7.2	500	FAAS	Food, fertilizer, soil and water samples	[13]
Pb(II), F**e(III),** Cd(II), Au(III), Pd(II), Ni (II)	Cu-II rubeanic acid	0.14	12.5-2.5	FAAS	Water, soil, and sediment samples	[14]
Pb(II), **Fe(III)**	Violiric acid-Cu II	0.18	50-100	FAAS	Sea and mineral waters, urine, soil and physiological solution	[15]
Fe, Mn, Co	$Mg(OH)_2$	-	26	ICPMS	ocean water	[16]
Fe(III) and nine element ion	Cu-II-9-fenil-3-floron	12.9	30	FAAS ICPMS	Water, sediment	[17]
Cr(III), **Fe(III)**, Pb(II), Zn(II)	POHBAT free carrier element	0.7	10	FAAS	Environmental sample	[18]

Continued in Table 10

Analytes	**Collector**	**Fe detection limit, µgL^{-1}**	**CF***	**Instrument**	**Sample**	**Reference**
Fe and twenty-six elements	$InPO_4$	0,20	10-30	ICP-AES	Commercial salt	[19]
Fe(III), Pb, Cu(II)	Cu-II-salisildoxim, Ni-II-salisildoxim	1.6	20	FAAS	Water samples	[20]
Pb,Co, Cu,Cd, **Fe**, Ni	$Zr(OH)_4$	1.53	25	FAAS	Natural water, tea, coffee, tabocca and fish samples	[21]
Fe	$Mg(OH)_2$	0.005	10	ICP-MS	Ocean water	[22]
Cd(II), Cr(III) CoII, Cu(II), **Fe(III),** Pb(II), Mn(II)	CTAB free carrier element	2.1	10	FAAS	Natural water and soil samples	[23]
Co, Pb, Cu, **Fe** ve Zn	Ni(II)-2-nitroso-1-naftol-4-sülfonic acid	1.38	25	FAAS	Environmental sample	[24]
Pb(II), **Fe III,** CoII ,Cr(III), Zn	Cu-BPHA	2.3	150	FAAS	Natural water, hair, urine, soil, sediment and peritoneal fluids samples	[25]
Cu(II), Co(II), Cd(II), Ni(II), Mn(II), **FeIII**, Pb(II),	$Tm(OH)_x$ (Tulyum hidroksit)	0.50	120	FAAS	Food and environmental samples	[26]
FeIII, Cr(III), Co(II), Pb(II), Zn(II)	Cu(II)-BPHA	0.67	100	FAAS	Food samples	[27]
Cu(II), Pb(II), Zn(II), **FeIII**, Cr(III)	BCP (free carrier element)	0.91	25	FAAS	Water and food samples	[28]
Fe	**$Mg(OH)_2$**	**10**	**10**	**UV-VIS Spek.**	**Tab water, mineral water, Rennie antiacid tablet**	**This work**

a Concentration faktör
b not given

There are some istrument like ICP-AES which can determine a concentration value with no need for preconcentrating while preconcentrating is essential to be determined by using an UV-VIS spectrophotometer. Another factor which affects the sensitivity is preconcentration factor. The preconcentration factor of the proposed method is 10. This value is the same with 10 of the studies in Table 3.8 while it is lower than the others. While it is possible to increase this value by reducing the final volume below 5 mL in the AAS, it is difficult in in the UV-VIS spectrophotometer.

4. CONCLUSION

The proposed method can be applied to tap water, mineral water, and antiacid tablets. This method can also be recommended for other water samples with metal pollution in which the copper concentration is not higher than that of the iron. High-grade interference in Cu (II) is not observed in atomic spectrometric methods such as AAS and AES. However, the hardware cost of these devices is about five times that of an UV-VIS spectrophotometre and may not be available in most analytical laboratories. The proposed method can be employed by the corporations/institutions with shoestring budgets that cannot afford to purchase such analytical devices more expensive than an UV-VIS spectrophotometer.

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