SOLOCHROME YELLOW 2GS AS ORGANIC REAGENT FOR SPECTROMETRIC DETERMINATION OF IRON(III)

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A rapid, reliable and inexpensive method for the direct determination of Fe (III) with the organic reagent Solochrome Yellow 2GS (disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid) is reported. In a 5-fold excess over Fe (III) concentration the organic reagent, **R** form with Fe (III) within pH range 2.79-3.00 a 1:2 (Fe:**R**) stable complex. The value of the total stability constant $\beta_s = 3.023 \cdot 10^5 \pm 1.55 \cdot 10^5$ $L^2 \cdot mol^{-2}$ was determined, which indicates the formation of a rather stable complex.

On this basis a spectrometric method for the quantitative determination of traces of iron (III) was proposed. The method is sensitive, accurate and reproducible, being characterized by a detection limit of 0.11 mg·L^{-1}, a linearity range between 0.3-5.0 μg·mL^{-1}, a recovery of 98.45 % ± 1.38 %, as well as a good repeatability and reproducibility, characterized by relative standard deviations of 1.537% and 1.365%, respectively. This method was applied in order to determine the iron contents in samples of drinking water and natural mineral water.

INTRODUCTION

The marked trend of phenols to form colored iron (III) compounds constitutes the basis for the use of a large number of phenol derivative compounds as spectrometric reagents to determine iron (III) by means of visible molecular absorption methods;[1] for instance: salicylic acid,[2] 5-sulphosalicylic acid,[3] Tyrone,[4] nitrosophenols,[5] azo-compounds,[6] N,N'-bis(2-hydroxyphenylmethyl)-N,N'-bis(2-pyridilmethyl)-1,2-ethanediamine,[7] ethylenediamine-*N,N'*-bis(2-hydroxyphenyl)acetic acid (EDDHA),[8] resorcylic acid (2,4-dihydroxybenzoic acid, DHB)[9] and N,N'-bis-(2-hydroxy-5-bromobenzyl)-2-hydroxy-1,3-diiminopropane.[10]

The organic reagent disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid, noted hereinafter **R**, is known under the commercial name of Solochrome Yellow 2GS whose formula is presented in Fig. 1.
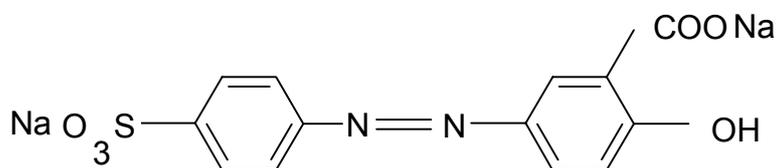

Fig. 1 – The formula of the organic reagent **R**.

According to the data existing in the literature, the reagent **R** may build complex combinations with several ions: Cu (II), Ni (II), Co (II),[11] Cd (II), Zn (II),[12] La (III) and Nd (III).[13]

The interaction of the reagent **R** with Cd (II) and Zn (II), in aqueous solution was polarographically studied in the presence of Me$_4$NClO$_4$ at 25ºC, 35ºC and 45ºC.[12]

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The kinetics of building mixed complexes further to the reaction between chromium (III) nitrilotriacetate and the reagent **R** was studied in the presence of $NaClO_4$ at 5-7ºC and 40ºC and at an ionic strength of the solution of 0.1 mol·L^{-1}. [14]

The stability constant of the complex combination of copper (II) with the reagent **R** was determined by means of spectrometric studies.[15] The effects of substitutes on the stability constants were discussed. The stability constants of the complexes formed by the reagent with Cu (II), Ni (II) and Co (II) [11] were also spectrometrically determined.

This work presents the results of a spectrometric study on the interaction between iron (III) and the disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid. Based on the obtained results a method for spectrometric determination of iron (III) was established. This method was validated and applied in order to determine the iron contents in assays of drinking water and mineral water.

EXPERIMENTAL PART

Reagents

All chemicals used were analytical reagent grade: Solochrome Yellow 2GS (Leeds, U.K.) and aqueous solution 10^{-3} M; $FeCl_3$ (Merck) and aqueous solutions 10^{-3} M and $5·10^{-4}$ M, both in HCl 10^{-1} M solution; $NiCl_2$ (Merck) and aqueous solution 10^{-3} M; $Co(NO_3)_2$ (Merck) and aqueous solution 10^{-3} M; $CuSO_4$ (Merck) and aqueous solution 10^{-3} M; $UO_2(NO_3)_2$ (Merck) and aqueous solution 10^{-3} M; $Pb(NO_3)_2$ (Merck) and aqueous solution 10^{-3} M; HCl (Merck) 30%, $\rho = 1,15$ g/cm^3 and aqueous solution 10^{-1} M; NaOH Titrisol (Merck) 1 M and aqueous solution 10^{-3} M.

Apparatus

The UV-VIS studies were performed using a JASCO V 530 spectrometer having 1 cm quartz cells. A Consort P 901 pH-meter (Tumhout, Belgium) provided by a combination electrode was used. The studied cations were quantitatively determined by means of an atomic absorption spectrometer Nova A 300 (Analytik Jena, Germany).

Procedure

The solutions to be studied were prepared in 25 mL calibrated flasks were exactly measured volumes of 10^{-3} M Fe (III) in 10^{-1} M hydrochloric acid and 10^{-3} M reagent **R** solutions were introduced; a calculated volume of HCl solution of known concentration was added to obtain a determined pH. The flasks were filled up to the mark with distilled water. Absorbance of each solution was measured against a corresponding Fe (III) free reagent blank, similarly prepared.

RESULTS AND DISCUSSION

The influence of wavelength, pH, amount of organic reagent and concentration of iron (III) on the absorbance was studied in order to establish the optimal working conditions for the quantitative determination of Fe (III).

The organic reagent Solochrome Yellow 2GS forms instantaneously, at room temperature with Fe (III) a complex, soluble in water.

Absorption spectra

The absorption spectra of the complex and of the organic reagent **R** are shown in Fig. 2. The maximum absorbance of the complex solution is at $\lambda = 490$ nm, while the solution that contains only reagent has a low absorbance.

All absorbance measurements were performed at $\lambda = 490$ nm against a corresponding blank reagent.

The effect of pH on the absorbance of the compound

In order to establish the influence of the pH of the solutions on the compound spectra, solutions containing 1 mL 10^{-3} M Fe^{3+} in 10^{-1} M hydrochloric acid and 5 mL 10^{-3} M reagent **R**, having various pHs between 2 and 4 were prepared in 25 mL calibrated flasks.

The absorbance of each solution was measured at $\lambda = 490$ nm as compared to a blank assay that contained 5 mL 10^{-3} M **R** in solution having the same pH as the sample. As it may be seen in Fig. 3 the complex absorbance increases with pH increase, reaching the maximum value within pH range 2.79-3.00 and then decreases. Further on, a 10^{-3} M reagent solution was used within pH range of 2.5-3.0.

Stoichiometry of the complex

The effect of reagent concentration was examined by measuring the absorbance of the solutions containing a known concentration of Fe (III) and different amounts of organic reagent **R** at pH ~ 2.79 - 3.00. The curve obtained (Fig. 4) shows a 1: 2 molar ratio Fe (III): **R** and a small excess of reagent over iron is required in order to obtain a maximum constant absorbance. The spectrometric titration using a constant amount of organic reagent **R** and variable concentrations of iron (Fig. 5), as well as Job's method (Fig. 6) show also a 1: 2 molar ratio Fe (III): **R**.
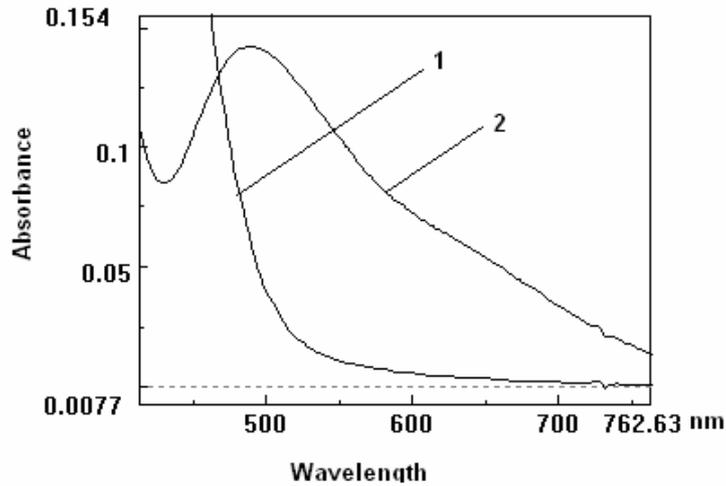
Fig. 2 – Absorption spectra:
1– reagent solution against water (4 mL 10^{-3} M R; 25 mL calibrated flask);
2– complex against blank reagent solution (1 mL 10^{-3} M Fe^{3+}/ 10^{-1} M HCl + 4 mL 10^{-3} M R; 25 mL calibrated flask).
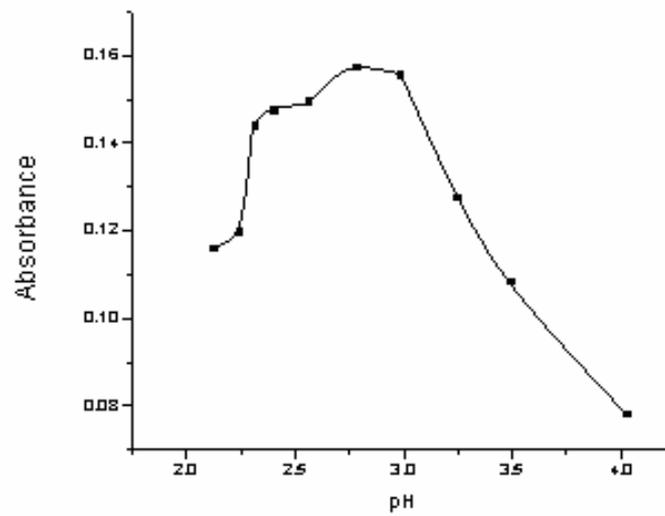

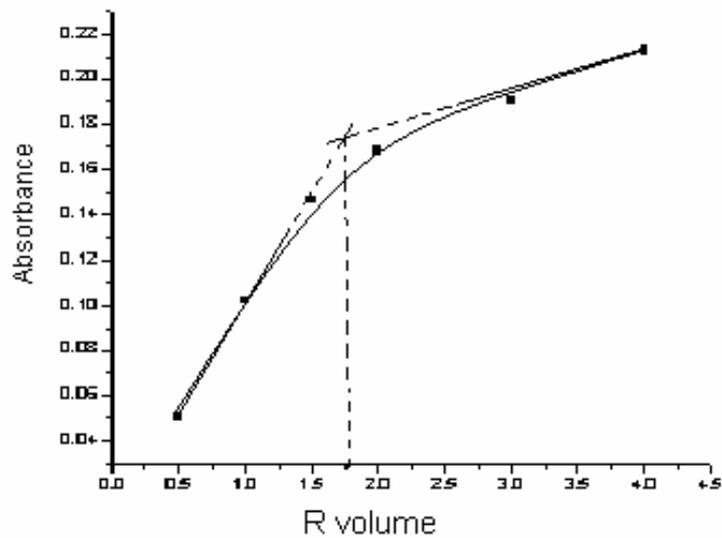Fig. 3 – Effect of pH on the absorbance of the complex (λ = 490 nm).

Fig. 4 – Spectrometric titration of Fe^{3+} by reagent solution
(samples: 1 mL 10^{-3} M Fe^{3+}/ 10^{-1} M HCl + V mL 10^{-3} M R; pH ~ 2.5; 25 mL calibrated flask; λ = 490 nm).
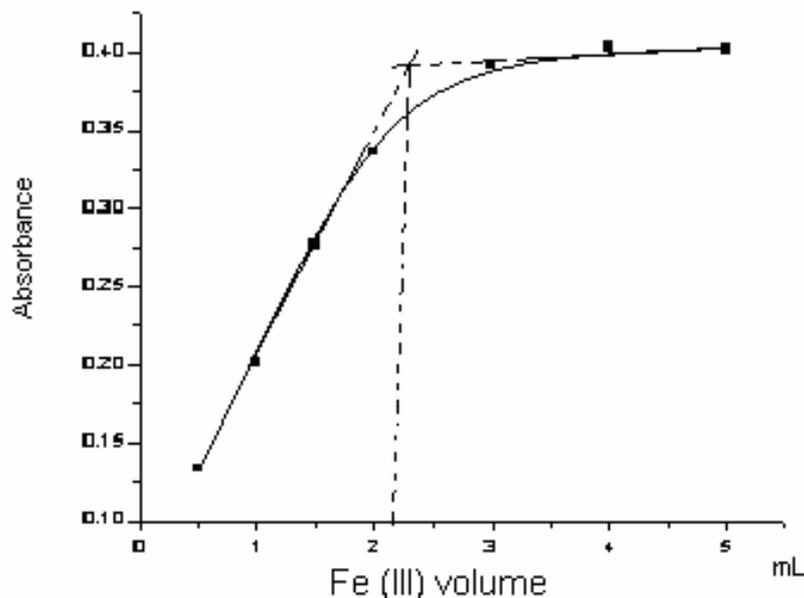
Fig. 5 – Spectrometric titration of the reagent by iron (III) solution (samples: 4 mL 10^{-3} M R + V mL 10^{-3} M Fe^{3+}/ 10^{-1} M HCl; pH ~ 2,5; 25 mL calibrated flask; λ = 490 nm).

a   b
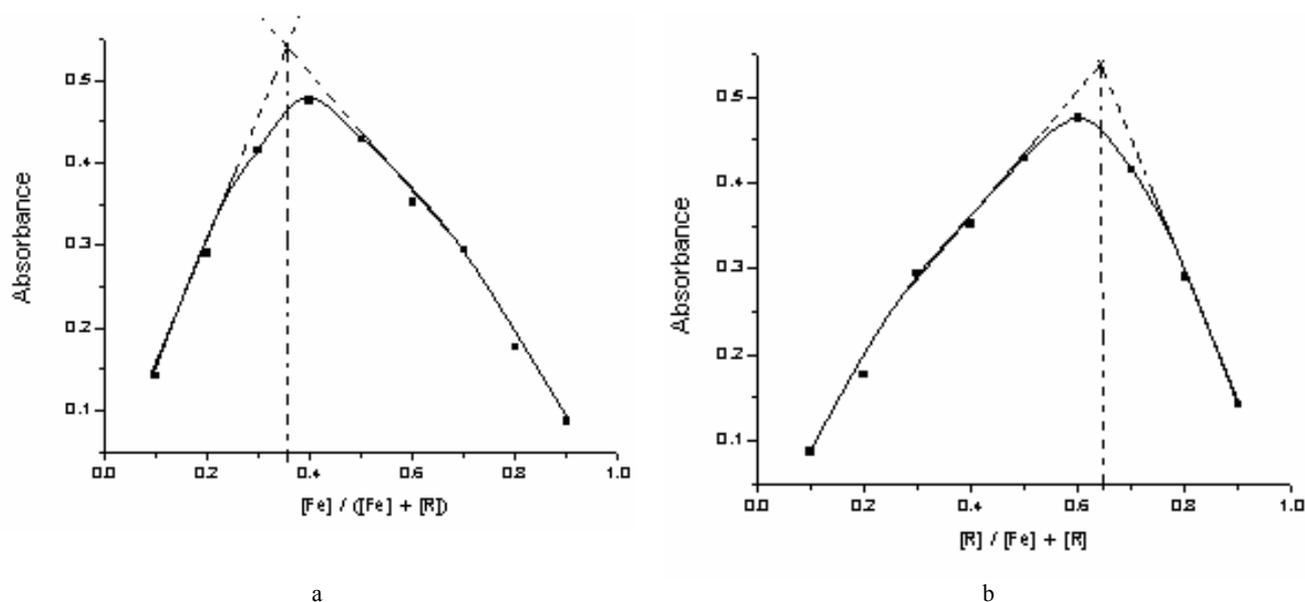
Fig. 6 – Determination of the molar ratio by Job's method
(10^{-3} M solutions of **R** and Fe^{3+}; pH ~ 2,5; 25 mL calibrated flask; λ = 490 nm):
a. A = f (molar fraction of iron) curve; b. A = f (molar fraction of the reagent) curve.

Stability constant

The stability constant of the complex combination resulting from the reaction between reagent and iron (III) was calculated from data obtained using the Job method. Three series of nonisomolar solutions, containing a fixed total number of moles of Fe (III) and organic reagent **R**, but in which the ratio Fe: **R** is systematically varied from large to small were used. The experimental conditions for determination and evaluation of the stability constant of the complex

formed between Fe (III) and organic reagent **R** are favorable to the formation of the most stable complex within pH range of 2.5-3.0 with a 1: 2 molar ratio. The formation of this compound in solution is complete at the inflexion point corresponding to the stoichiometric ratio (Fig. 7). The average value of the stability constant is β_s = $3.023 \cdot 10^5 \pm 1.55 \cdot 10^5$ L$^2 \cdot$mol^{-2} (Table 1). The value of the stability constant obtained at 20 ± 2°C shown a very stable complex in acidic solution (pH range of 2.5-3.0), for the corresponding stoichiometry.
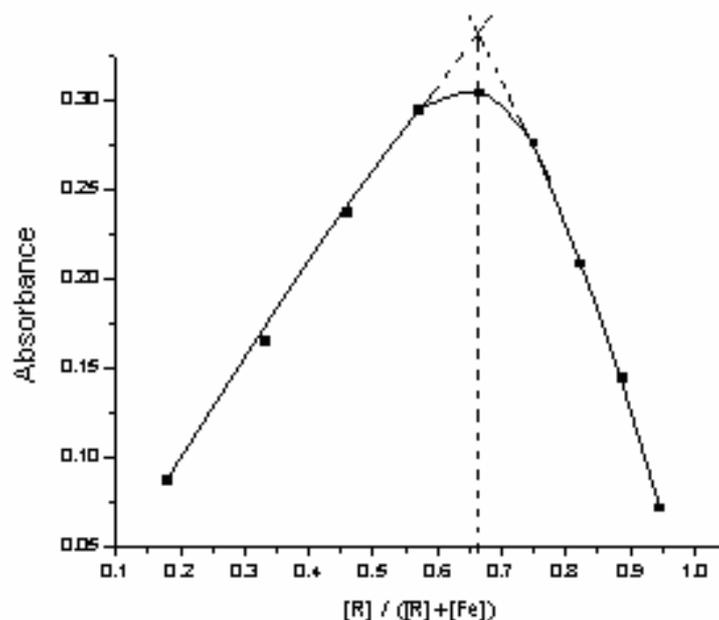
Fig. 7 – Experimental data for determination of instability constant
(solutions: 10^{-3} M reagent and $5 \cdot 10^{-4}$ M Fe^{3+}/ 10^{-1} M HCl; pH ~ 2,5; 25 mL
calibrated flask; λ = 490 nm).

Table 1

Experimental data for the calculation of the total stability constant β_s.

C M	p	X_{max}	β_s $L^2 \cdot mol^{-2}$	
$5 \cdot 10^{-4}$	2	0.66	$1.52 \cdot 10^5$	
$5 \cdot 10^{-4}$	2	0.65	$4.62 \cdot 10^5$	$3.023 \cdot 10^5$
$5 \cdot 10^{-4}$	2	0.655	$2.93 \cdot 10^5$	$\pm 1.55 \cdot 10^5$

Linearity of the method

All the absorbance measurements were performed at λ = 490 nm against a corresponding blank reagent (within pH range of 2.8-3.0). The calibration curve was obtained by plotting the absorbance value against the concentration of the solution. A linear relationship was obtained for iron (III) concentrations between 0.3-5.0 mg·L^{-1}. The equation of absorbance, A against concentration, C was: $A = 0.00431 + 0.06197 C$ with r = 0.99559. The values obtained for linearity show that the proposed method is free from procedural errors. The detection limit experimentally determined according to the ICH rules[16-17] is 0.11 mg·L^{-1}.

The molar absorbance coefficient was calculated as being: ε = 3750 L· mol^{-1}· cm^{-1}.

Accuracy of the method

In order to establish the accuracy of the method, six samples having 2.23 mg·L^{-1} as known iron (III) concentration were analyzed. The iron (III) concentration was initially determined from each sample under analysis. The results obtained are: mean 2.238 mg·L^{-1} and the standard deviation, SD = 0.02 mg·L^{-1}. Then, a set of assays having various amount of iron (III) was prepared through an addition to each sample of a known quantity of iron (III); the iron (III) concentration was determined from each assay being prepared as such. The data for the recovery studies presented in Table 2 show that the accuracy of the proposed method is characterized by a recovery between 98.73% and 100.6%.

Precision of the method

The precision of the proposed method, expressed by reproducibility and repeatability, was determined through the application of the method on samples with known iron (III) content.

Table 2

Determination of the accuracy of the method

Sample No.	Amount of Fe present in sample mg·L^{-1}	Amount of Fe added in sample mg·L^{-1}	Amount of Fe found in sample mg·L^{-1}	Recovery %
1	2.240	0.558	2.790	99.71
2	2.464	0.558	3.041	100.6
3	2.688	0.558	3.217	99.10
4	2.912	0.558	3.426	98.73
5	3.128	0.558	3.661	99.32
6	3.351	0.558	3.915	100.1

Repeatability was established based on the analysis of 6 samples having 2.23 mg·L^{-1} as known iron (III) concentration. The determination of iron concentration in each sample being made by the same analyst during the same day. For Fe (III) concentration the following values were obtained: 2.357, 2.398, 2.353, 2.380, 2.478 and 2.296 mg·L^{-1}. Based on experimental data, average value of 2.377 mg·L^{-1}, standard deviation SD = 0.06 and relative standard deviation RSD = 1.537 % were calculated. The results obtained show a good repeatability of the method.

Reproducibility was studied based on the determination of iron (III) concentration in two series each made up of 6 samples and 2.23 mg·L^{-1} concentration of iron (III) by two different analysts in different days; the following Fe (III) concentrations were obtained: 2.330, 2.367, 2.441, 2.341, 2.380 and 2.303 mg·L^{-1}, and respectively 2.419, 2.404, 2.393, 2.372, 2.383 and 2.383 mg·L^{-1}. Based on the experimental data, average value of 2.376 mg·L^{-1}, with a standard deviation SD = 0.03 and a relative standard deviation RSD = 1.365% were calculated.

Interferences

In order to establish any possible interferences, the UV-VIS spectra were recorded for solutions containing one of the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, $(UO_2)^{2+}$ in the working conditions established as optimal for iron (III) determination (Fig. 8).
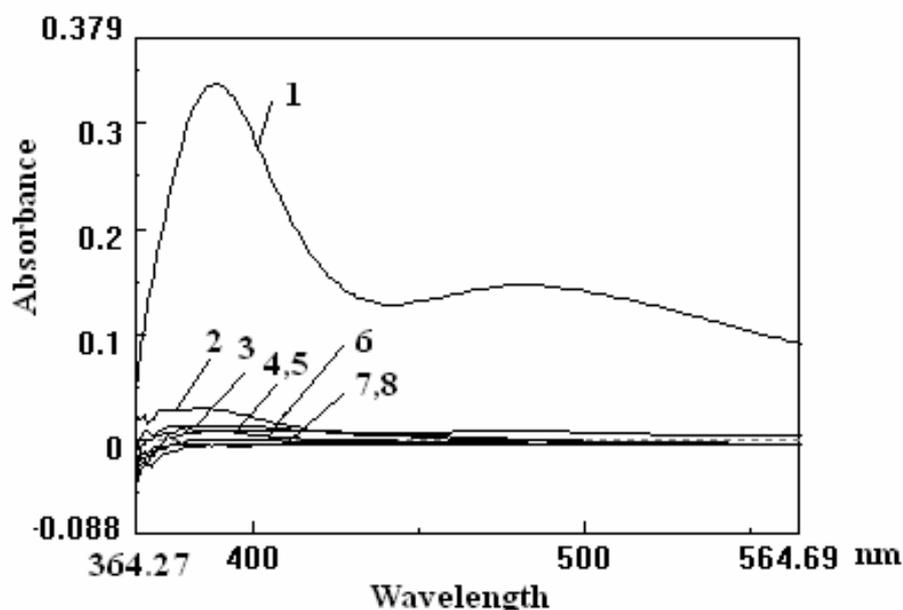

Fig. 8 – Absorption spectra of following ions in the presence of the organic reagent Solochrome Yellow 2GS at *p*H 2.79 - 3.0: 1– Fe (III); 2– Fe (II); 3– U (VI); 4– Cu (II); 5– Zn (II); 6– Ni (II); 7– Co (II); 8– Pb (II); (25 mL calibrated flask).

The effect of potential interfering ions on the determination of iron (III) with the organic reagent

Solochrome Yellow 2GS (disodium salt 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic) at λ = 490 nm

within pH range 2.79-3.00 was investigated by adding known concentration of each ion to a solution containing 4.46 mg·L⁻¹ iron (III). The ions: Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, $(UO_2)^{2+}$ do not interfere when being in equal or lower concentrations than those of iron (III). Fe^{2+} do not interfere even in a 2-fold excess over Fe^{3+} concentration. It was found that: Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+} do not interfere at all.

Practical applications

The spectrometric method proposed for the quantitative determination of iron (III) with the organic reagent Solochrome Yellow 2GS was applied on real samples of drinking water and of Harghita natural mineral water existing on the market. In the case of FAAS[18] analysis the method of standard additions was used, because the Fe (III) concentration in water is very low according to the quality certificate for the natural mineral water and to the international standards[19] for drinking water.

The results presented in Table 3 show a good agreement between the values determined by the proposed method, those given through the application of FAAS method, as well as those written down on the quality bulletin of the commercial natural mineral water.

Table 3

Iron content determination in water samples

Sample	Concentration of Fe (III) written on the quality certificate mg/L	Concentration of Fe (III) determined by proposed method mg/L	Concentration of Fe (III) determined by FAAS[18] mg/L
Natural mineral water *Harghita*	< 0.3 (according to the quality certificate)	0.272	0.254*
Tap water	<0.3 (according to the international standards[19])	0.244	0.220*

Notes: Each result is the means of 6 determinations. * Standard additions method was used.

CONCLUSIONS

A rapid, reliable and inexpensive method for the direct determination of Fe (III) with the organic reagent Solochrome Yellow 2GS (disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic)   is reported. In a 5-fold excess over Fe (III) concentration, the organic reagent, **R** form with Fe (III), within pH range 2.79-3.00, a 1: 2 (Fe: **R**) stable complex. On this basis a spectrometric method for the quantitative determination of traces of iron (III) was proposed.

The value of the total stability constant $\beta_s = 3.023 \cdot 10^5 \pm 1.55 \cdot 10^5$ $L^2 \cdot mol^{-2}$ was determined, which indicates the formation of a rather stable complex.

The proposed method is sensitive, accurate and reproducible, being characterized by a detection limit of 0.11 mg·L⁻¹, a linearity range between 0.3 - 5.0 µg·mL⁻¹, a recovery between 98.735% and 100.6%, as well as a good repeatability and reproducibility, characterized by relative standard deviations of 1.537% and 1.365%, respectively.

The spectrometric method proposed for the quantitative determination of iron (III) with the organic reagent Solochrome Yellow 2GS was applied with good results on real samples of drinking water and of Harghita natural mineral water existing on the market.

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