

Flow Injection Spectrofluorimetric Determination of Iron in Industrial Effluents based on Fluorescence Quenching of 1-Naphthol-2- Sulfonate

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Abstract A sensitive and selective spectrofluorimetric method has been developed for flow injection analysis (FIA) of iron(III) based on its fluorescence quenching effect on the water soluble 1-naphthol-2-sulfonate. The fluorescence emission spectra were collected with excitation at 283 nm. The emission peaks of the neutral and anionic forms of 1-naphthol-2-sulfonate as well as the band area were found to decrease linearly with iron(III) concentrations over the range 0.1–18 $\mu\text{g ml}^{-1}$ and a detection limit of 3.4 ng ml^{-1} (emission at 349 nm) with FIA. Possible interferences from different cations and anions, which could affect the analytical response, are evaluated and showed the high selectivity of the method. The effect of solution pH and 1-naphthol-2-sulfonate concentration were examined and the reaction conditions are optimized. The method is successfully applied to determine iron(III) in industrial effluents from different sources without any complications with recoveries of almost 100% with both manual and flow injection methods. Results were found to be very consistent with those obtained using atomic absorption spectrometry.

Keywords Fluorescence quenching · Flow injection · Naphthol derivatives · Determination of iron(III) · Industrial effluents

Introduction

Iron is found in many natural and treated waters. It is an objectionable constituent in both domestic and industrial water supplies. Iron is not preferable to be present in raw materials required for the manufacture of glass, crystal and ceramics (porcelain, alumina refractories and refractory mortars) in which iron concentration may be at maximum of 0.1%. High concentrations in surface waters can indicate the presence of industrial effluents or runoff from other operations. Because of this, iron determination in environmental and industrial samples with such low levels precisely, rapidly and accurately is of paramount importance. Many analytical methods were reported for the determination of iron; they are inductively coupled plasma mass spectrometry [1], atomic absorption spectrometry [2, 3], potentiometry [4], ion chromatography [5], chemiluminescence [6], anodic stripping voltammetry [7] and spectrophotometry [8, 9]. However, reported spectrofluorimetric methods for the determination of iron(III) are rare. These methods depends mainly either on detecting the fluorescence emitted up on the formation of a metal chelate (direct fluorimetry) or following fluorescence quenching induced by the presence of the metal cation. In direct fluorimetry, some fluorogenic compounds were used for the determination of iron [10–16]. These methods suffer from different drawbacks as pre-treatment step such as pre-reduction, occurrence of metal interference or addition of surfactant as fluorescence enhancer. In fluorescence quenching methods, some other fluorogenic compounds

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were quenched by iron [17–20]. However, these methods also show serious interferences, narrow linear range or high detection limit. General characteristics of the reported fluorimetric methods are summarized (Table 1).

The flow injection analysis (FIA) method is a very useful technique for rapid determination of many samples because it can accomplish high sampling automatism with good precision. Moreover, FIA technique can make reproducible timing analysis, eliminate sample pretreatment and minimize solvent and reagent consumption. FIA equipped with a spectrofluorimetric detector seems to satisfy these requirements in addition to the low cost instrumentation and high sensitivity and selectivity of the fluorescence measurements.

In this paper, we study the fluorescence quenching of 1-naphthol-2-sulfonate (1-NOH-2-S) by iron(III) in aqueous medium because it is highly water soluble, emissive in both its neutral and anionic forms with comparable intensities, the fluorescence quantum yield is relatively high and due to its high sensitivity to bind to iron(III). The influence of reaction variables and the effect of interfering ions are studied. This procedure was applied to the determination of trace amounts of iron with long-term stability, remarkable selectivity and applicability for manual and flow injection modes of operation. Determination of iron in industrial effluent samples without the need for pre-concentration, pre-separation or organic solvent extraction is also concerned.

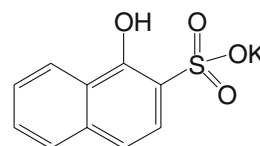
Experimental

Apparatus

All luminescence measurements were made with an LS-50B luminescence spectrometer (Perkin Elmer) equipped with a 20 k watt Xenon discharge lamp. All pH adjustments were made with an EDT instruments (DR 359 TX Ion concentration–pH meter) pH meter. Absorbance measurements were carried out using Unicam UV2-300 UV/Visible spectrometer version 4.15.

Materials and Reagents

The potassium salt of 1-naphthol-2-sulfonate (1-NOH-2-S) was purchased from Kodak and purified as in the literature [21]. Purity was checked by UV and fluorescence spectroscopy. Doubly distilled water was used.



1-naphthol-2-sulfonate (1-NOH-2-S)

Buffer solution (universal) was prepared in 1 l measuring flask by dissolving 2.47 g H_3BO_3 , 2.4 ml CH_3COOH and 2.7 ml H_3PO_4 and completing to the mark with bi-distilled

Table 1 General characteristics of some fluorimetric methods for the determination of iron(III)

| Reagent | Linear range $\mu\text{g/ml}$ | Det. limit ng/ml | Working pH | Serious Interference (M^{n+}/Fe^{3+}) | FIA | $\lambda_{ex}/\lambda_{em}$ | Ref. |
|---|-------------------------------|---------------------------|--------------------|--|---------|-----------------------------|------|
| 1-NOH-2-S | 0.1–18 | 3.4 | 6–8 | Table 2 | 120 s/h | 283/349 | PM* |
| 4-hydroxyquinoline | 0.28–0.56 | 168 | 12–13(≥ 12) | Mn^{2+} (0.06:1), Cu^{2+} and Hg^{2+} (0.2:1), Co^{2+} (0.6:1), Cd^{2+} , Pb^{2+} , Mo^{4+} , Zn^{2+} (1:1), Ca^{2+} (2:1) | N.A. | 305/380 | 18 |
| 2-pyridinecarbaldehyde-5-nitro-pyridyl-hydrazone | 0.2–1.45 | 28 | 6.75–7.75 | Fe^{2+} (0.3:1), Cu^{2+} (0.1:1), Pd^{2+} (0.5:1), Cd^{2+} and Al^{3+} (1:1), Zr^{4+} and Sc^{3+} (3:1), Pt^{2+} (4:1) | N.A. | 300/410–420 | 12 |
| salicylic acid | 0.056–0.56 | 2.8 | 8.5 (>8) | Fe^{2+} (7:1), Co^{2+} , Sm^{3+} and Y^{3+} (10:1), Cr^{3+} and Pb^{2+} (20:1) | N.A. | 299/409 | 19 |
| 5-(4-methylphenylazo)-8-aminoquinoline | 0.01–0.7 | 10 | ≤ 2 | Mn^{7+} , Pd^{2+} (0.05:1), Sn^{2+} , Ce^{4+} and Cr^{6+} (2:1), Hg^{2+} and W^{6+} (4:1), V^{5+} (5:1), Au^{3+} (7:1), Zr^{4+} (9:1), Ag^+ (12:1), Bi^{3+} and Mo^{6+} (25:1) | N.A. | 316/528 | 13 |
| 5-(4-methoxy-phenylazo)-8-(4-toluenesulfonamido)quinoline | Up to 0.17 | 0.12 | ≤ 2 | Au^{3+} (10:1), Zr^{4+} and Bi^{3+} (20:1), V^{5+} , Pd^{2+} and Ag^+ (30:1), Mo^{6+} (40:1), Sb^{3+} (60:1) | N.A. | 317/534 | 14 |
| Quercetin, self ordered ring technique | 0.005–0.150 | 1.39 | 7.3 | Cu^{2+} (0.1:1), Mn^{2+} (0.15:1), Fe^{2+} and Co^{2+} (0.25:1), Cd^{2+} (0.5:1), Pb^{2+} (1:1), Mg^{2+} , Al^{3+} , Hg^{2+} and Zn^{2+} ($\approx 2:1$) | N.A. | 450–480/500–800 | 20 |

PM* proposed method

water. To 100 ml of the above solution, an appropriate volume of 0.2 M NaOH was added to get the desired pH.

The FIA system is shown (Fig. 1). The carrier solution was propelled by means of the peristaltic pump, Ismartic MS-reglo, through Tygon tubing (0.64 mm i.d.) at the desired flow rate. A manual injection valve (Rheodyne, model 7125) fitted with a 100 μL sample loop was used for sample injection as previously discussed [22]. Atomic absorption spectrometric measurements were made with Perkin-Elmer AAS spectrometer (model 3100) and the optimum conditions were adjusted according to the instrument manual [23].

General Procedure

Aliquots of iron(III) stock solutions containing (1–25 $\mu\text{g ml}^{-1}$) were transferred to 10 ml volumetric flasks followed by 1.0 ml of 60 $\mu\text{g ml}^{-1}$ of 1-NOH-2-S reagent. The solutions were completed to the mark with a universal buffer of pH 8. The decrease in the reagent's fluorescence as a function of iron(III) concentration was measured. In the FIA mode, the peristaltic pump was used to pump equal volumes of 1-NOH-2-S reagent and the carrier buffer (pH 8) through the system. The sample was injected through an injector loop (100 μl) to a mixing tee where it was mixed with 1-NOH-2-S reagent at room temperature. The fluorescence spectra were measured by setting the excitation monochromator to 283 nm with excitation and emission bandwidth to 5 nm and calibration curve was plotted according to Stern-Volmer relationship.

Applications

Grab samples were collected from the industrial effluents of some industries (metal processing and textile) and from drainage canals then filtered using 0.45 micron glass filter membrane. In order to determine the content of total iron as iron (III) in a sample, any traces of iron (II) have to be first oxidized to iron (III). A 1 ml aliquot of the filtrate was transferred to a 50 ml beaker, mixed with 2 ml of 30% H_2O_2 and boiled the solution for 5 min to attain complete oxidation of any iron (II) to iron (III) if present. The solution is then transferred to 50 ml flask and

the mixture was completed to the mark with bi-distilled water. A 1.00 ml aliquot of the test solution was transferred to 10 ml volumetric flask followed by 1.0 ml of 60 $\mu\text{g ml}^{-1}$ of 1-NOH-2-S reagent solution. The mixture was completed to the mark with universal buffer of pH 8. A blank experiment was made under identical conditions. The fluorescence intensity in the absence and presence of iron(III) were measured. Sample readings were compared to calibration curve to determine the exact concentration.

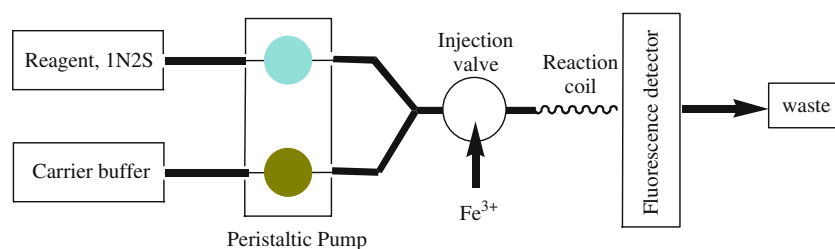
Results and Discussion

Spectral Characteristics of 1-naphthol-2-sulfonate

The excitation and emission spectra of 6.0 $\mu\text{g ml}^{-1}$ of 1-NOH-2-S in the presence and absence of 8 $\mu\text{g ml}^{-1}$ iron (III) are shown in Fig. 2 at pH=8.0. The fluorescence emission spectra were collected with 283 nm excitation wavelength, while the excitation spectra were recorded with 449 nm emission wavelength. It has been established that the emission from the anionic form is at lower energies than that of the neutral species [24–26].

Since 1-NOH-2-S has a pK_a of 9.58, essentially all ground state molecules will be fully protonated for a solutions at $\text{pH} < 7$ [26]. Irradiation of such a solution produces a substantially more acidic (pK_a^* of 1.58 [21, 26]) electronically excited state which transfer a proton to water producing an electronically excited anion. Upon excitation, 1-NOH-2-S gives two emission bands in water, one from the neutral molecule centered at 349 nm and a broad structureless band at 449 nm due to emission from the anion form (Fig. 2). It has been found that the fluorescence intensity of both peaks are quenched in the presence of iron (III), i.e., 1-NOH-2-S is quenched by iron (III) in its neutral or anionic forms. Even though no changes were observed in the absorption spectrum of 1-NOH-2-S upon the addition of iron (III) within the range of concentrations used in this work, addition of much higher concentrations of iron (III) results in an appearance of a new absorption band with a peak maximum at 501 nm with a shoulder at 380 nm and an isosbestic point at

Fig. 1 Schematic diagram of the flow injection system



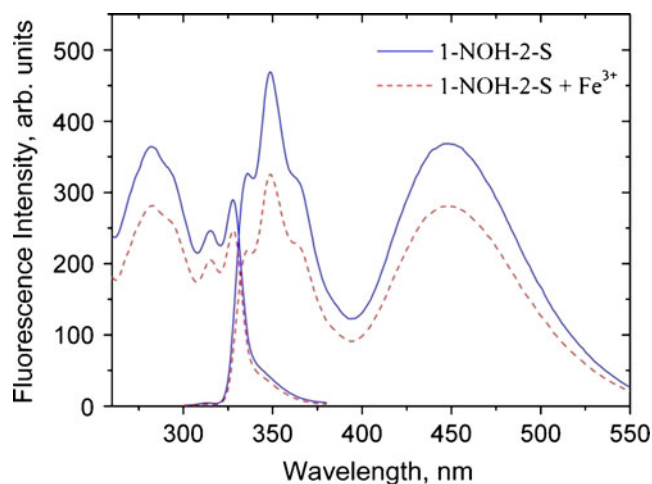


Fig. 2 The excitation and fluorescence emission spectra of 6.1 $\mu\text{g/ml}$ 1-naphthol-2-sulfonate at pH 8.0 in the absence and presence of 8 $\mu\text{g/ml}$ iron(III)

338 nm. Therefore, quenching of 1-NOH-2-S by iron (III) is believed to be static in nature.

Effect of pH

The effect of pH on the spectral characteristics of 1-NOH-2-S was studied over a wide range of pH values from 3 to 12. It has been found that upon changing the pH from 3 to 8, the emission of the neutral form was found to decrease slowly and then sharply from pH 8 to 10 and becomes very weak beyond pH 10. On the other hand, the emission of the anionic form increases slightly from pH 3 to 5 and becomes approximately constant over the pH range 5 to 8 and then decreases beyond 8 as shown (Figs. 3 and 4).

The pH effect on the fluorescence quantum yield of 1-NOH-2-S is shown (Fig. 5). The fluorescence quantum yield was found to increase slowly from pH 3 to 8 beyond

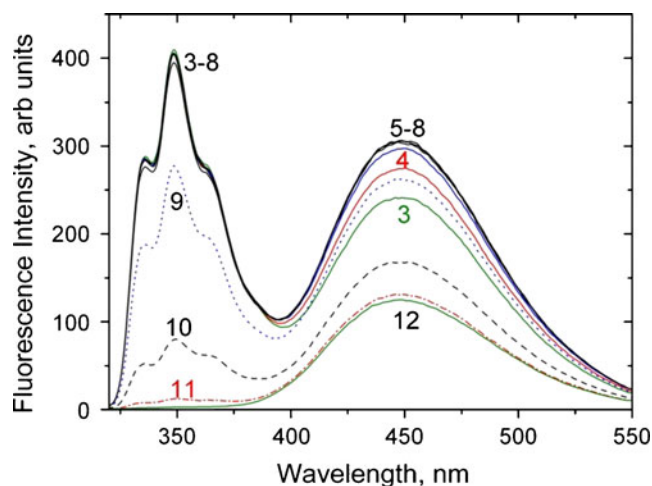


Fig. 3 The fluorescence emission spectra of 6.1 $\mu\text{g/ml}$ 1-naphthol-2-sulfonate at different pH values

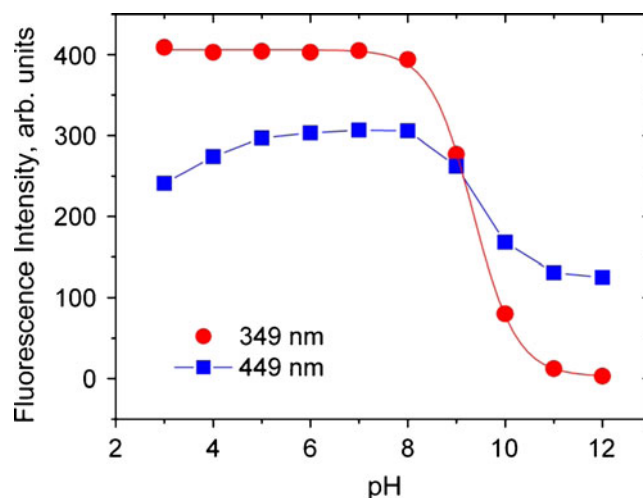


Fig. 4 Effect of pH on the fluorescence intensities of the neutral (349 nm) and anionic (449 nm) forms of 1-naphthol-2-sulfonate (6.1 $\mu\text{g/ml}$)

which it decreases sharply. The effect of pH on the fluorescence quantum yield was found to follow the trend of the anionic form but as sharp as that of the neutral form. Therefore the highest quantum yield was found to be in the pH range of 6–8.

Figure 6 shows the effect of pH on the quenching of 1-NOH-2-S by iron(III). It shows that the maximum value of Φ_0/Φ is at pH 8.0. Therefore pH=8.0 was chosen for the rest of measurements as it gives the highest value of the quenching ratio Φ_0/Φ and also the highest fluorescence quantum yield for 1-NOH-2-S.

Effect of 1-NOH-2-S Concentration

The variation of the quenching effect (F_0/F) was examined as a function of 1-NOH-2-S concentration (pH 8.0) in the presence of 8 $\mu\text{g ml}^{-1}$ iron(III). 1-NOH-2-S concentration

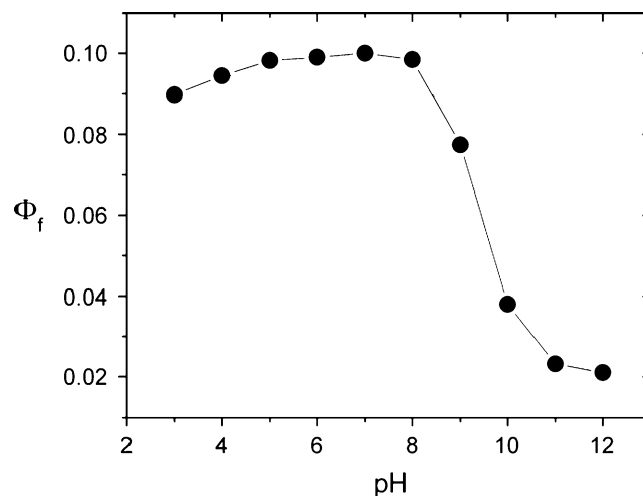


Fig. 5 Effect of pH on the fluorescence quantum yield of 1-naphthol-2-sulfonate (6.1 $\mu\text{g/ml}$)

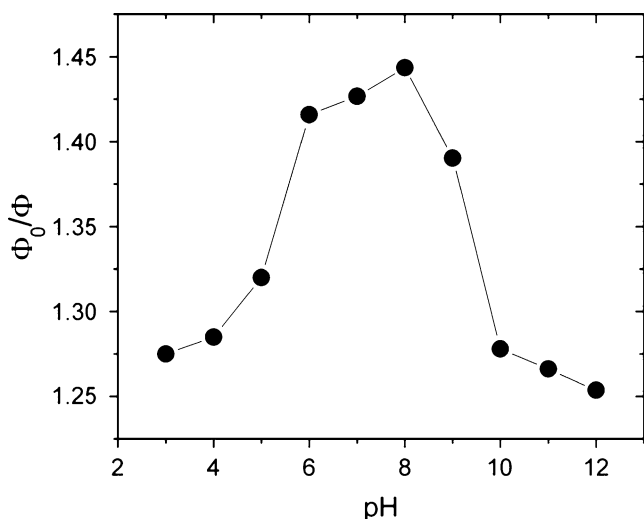


Fig. 6 The effect of pH on the quenching of 1-naphthol-2-sulphonate by iron(III)

was studied over a wide range from 0.1 to 23 $\mu\text{g ml}^{-1}$. It was found that the ratio F_0/F is about the same over the range of 0.1–8 $\mu\text{g ml}^{-1}$ and then decreases nonlinearly. Therefore 6.0 $\mu\text{g ml}^{-1}$ of 1-NOH-2-S was used for further studies.

Calibration Curve of Iron(III)

The effect of iron (III) concentration on the fluorescence quantum yield of 1-NOH-2-S at pH 8 was found to follow Stern-Volmer relationship [27]:

$$F_0/F = 1 + K_{SV}[Q]$$

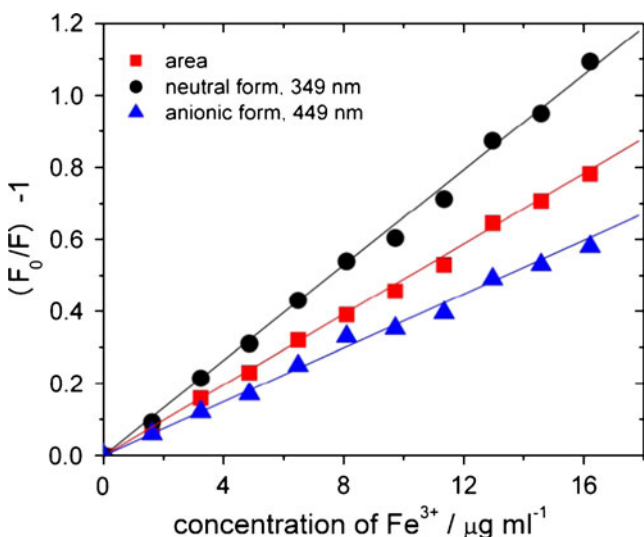


Fig. 7 Dependence of $(F_0/F)-1$ on the concentration of iron(III)

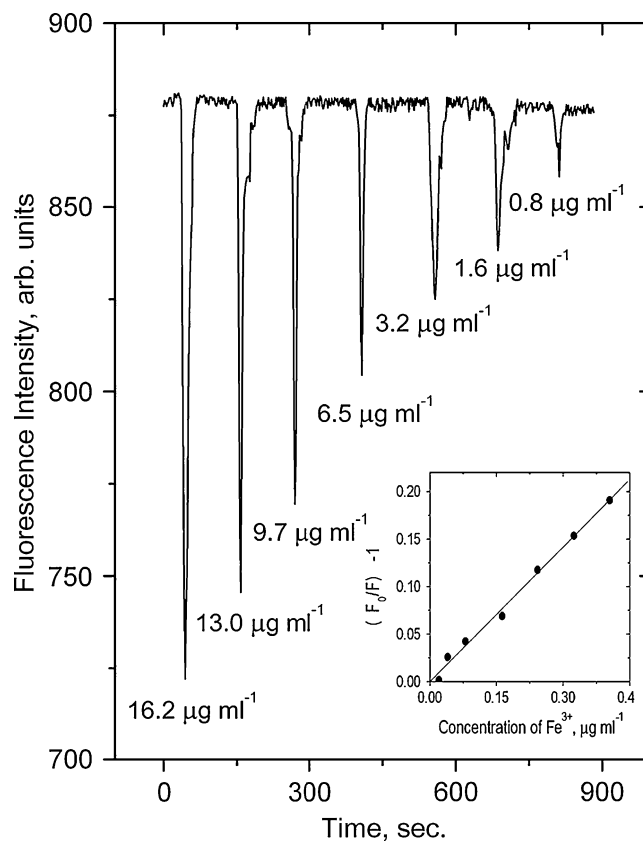


Fig. 8 Fluorescence Intensity as a function of time with different concentrations of iron(III) (Inset shows the Stern-Volmer plot for the collected data in graph)

where F_0 and F are the fluorescence quantum yields of 1-NOH-2-S in the presence and absence of the quencher, Q , respectively[27]. K_{SV} is the Stern-Volmer quenching constant.

Figure 7 shows the Stern-Volmer plot using 6.0 $\mu\text{g ml}^{-1}$ of 1-NOH-2-S at pH 8 following different emission wavelengths. It has been found the fluorescence of 1-NOH-2-S decreases linearly with increasing iron(III) concentration over the range 0.1–18 $\mu\text{g ml}^{-1}$. Data analysis was done following the peaks at 349 nm (neutral form), 449 nm (anionic form) and band area. It has been found that quenching of iron(III) is much more efficient on the peak due to the neutral form than that of the anionic form. The least squares regression analysis of these data gave a slope expressing K_{SV} of $0.066 \pm 0.002 \mu\text{g}^{-1} \text{ ml}$ following emission at 349 nm, $0.049 \pm 0.001 \mu\text{g}^{-1} \text{ ml}$ (area) and $0.037 \pm 0.001 \mu\text{g}^{-1} \text{ ml}$ (449 nm) with a correlation coefficient of 0.99 ($n=11$) and standard deviation as low as $\pm 0.5\%$. The lower limit of detection (LOD) calculated according to IUPAC recommendations [28]: $\text{LOD} = K S_0/S$ where S_0 is the standard deviation of the blank measurements ($n=5$), S is the slope of the calibration curve and K is a numerical factor depending on the degree of confidence level needed.

Table 2 Effect of foreign ions on the quenching of $6.1 \mu\text{g ml}^{-1}$ 1-naphthol-2-sulfonate for the determination of $1.6 \mu\text{g ml}^{-1}$ iron(III)

| Interfering ion | Tolerance ratio (w/w) |
|-------------------------------|-----------------------|
| Co ²⁺ | 55 |
| Ni ²⁺ | 1160 |
| Cu ²⁺ | 193 |
| Al ³⁺ | 193 |
| Cd ²⁺ | 260 |
| Zn ²⁺ | 930 |
| Mn ²⁺ | 170 |
| Ca ²⁺ | 520 |
| Ba ²⁺ | 4200 |
| Li ⁺ | 80 |
| Pb ²⁺ | 1300 |
| Fe ²⁺ | 600 |
| Mg ²⁺ | 2200 |
| NO ₃ ⁻ | 70 |
| SO ₄ ²⁻ | 490 |
| Br ⁻ | 170 |
| I ⁻ | 205 |

With $K=3$, the limit of detection of the proposed method was 45 ng ml^{-1} (at 349 nm) in the manual mode.

Flow Injection Analysis

The flow injection is applied on the proposed method at the optimized conditions of pH 8, an excitation wavelength of 283 nm and collecting emission at 349 nm. 1-NOH-2-S concentration used was $6 \mu\text{g ml}^{-1}$ and different concentrations of iron(III) were injected with 100 μl sample loop to cover the linearity range from 0.8 to $16.2 \mu\text{g ml}^{-1}$ with flow rate of 2.5 ml min^{-1} (Fig. 8). The linear regression analysis shown as an inset in Fig. 8 gives a slope of $0.472 \mu\text{g}^{-1} \text{ ml}$ and consequently a detection limit of 3.5 ng ml^{-1} can be obtained with standard deviation of $\pm 0.6\%$. The residence or peak times (T) for the lower (0.8 $\mu\text{g/ml}$) and the higher (16.2 $\mu\text{g/ml}$) detectable concentrations were 12 and 44 s.; respectively. The appearance times (t_a) were 6 and 34 s., while the decay

times (T') were 8 and 20 s.; respectively. Finally, the minimum times between injections (Δt) were 14 and 30 s; respectively which assures sample frequency of ≥ 120 sample/hr.

Effect of Foreign Ions

Under the optimized conditions, the effect of common cations and anions on the determination of $1.5 \mu\text{g ml}^{-1}$ iron (III) was examined and shown in Table 2 for those showing considerable interference. Effects of cations and anions were made with salt solutions containing their chloride and sodium counter ions, respectively. The tolerance limits of foreign ions were taken as the maximum amounts causing a change of $\pm 5\%$ in the fluorescence intensity. It can be seen that most of cations and anions examined do not interfere.

Applications

The method was applied to the determination of iron in industrial effluents from different resources. The sample solution was analyzed without a pre-concentration process (Table 3). The results are in a very good agreement with those obtained with FAAS.

Conclusion

A simple, sensitive and selective spectrofluorimetric method is employed to the determination of iron (III) both in the manual and flow injection modes of operation. Fluorescence quenching of 1-NOH-2-S has been found to be linearly correlated with iron (III) concentrations over the range $0.1\text{--}18 \mu\text{g ml}^{-1}$ in both manual and FIA modes. The method has shown a high selectivity as iron (III) can be detected in the presence of wide range of interfering ions. The method has applied to the determination of iron (III) in the effluent of some industrial activities with high precision. It has also been found that, the difficulties reported previously in similar studies have been avoided in the current study.

Table 3 Fluorimetric determination of iron(III) concentration ($\mu\text{g ml}^{-1}$) in the different samples collected and recovery% compared with atomic absorption method

| Sample | Proposed method | AAS | RSD,% ^a |
|---|-----------------|----------------|--------------------|
| Textile industrial effluents, (1) | 3.2 ± 0.1 | 3.1 ± 0.1 | 1.20 |
| Local textile industrial effluents, (2) | 2.3 ± 0.1 | 2.3 ± 0.1 | 1.50 |
| Suburban drainage canal | 2.0 ± 0.1 | 2.0 ± 0.1 | 1.60 |
| Local metal works industrial effluents | 1.5 ± 0.05 | 1.4 ± 0.05 | 0.60 |

^a Relative standard deviation ($n=3$)

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